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Rockwell International
Newbury Park, CA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

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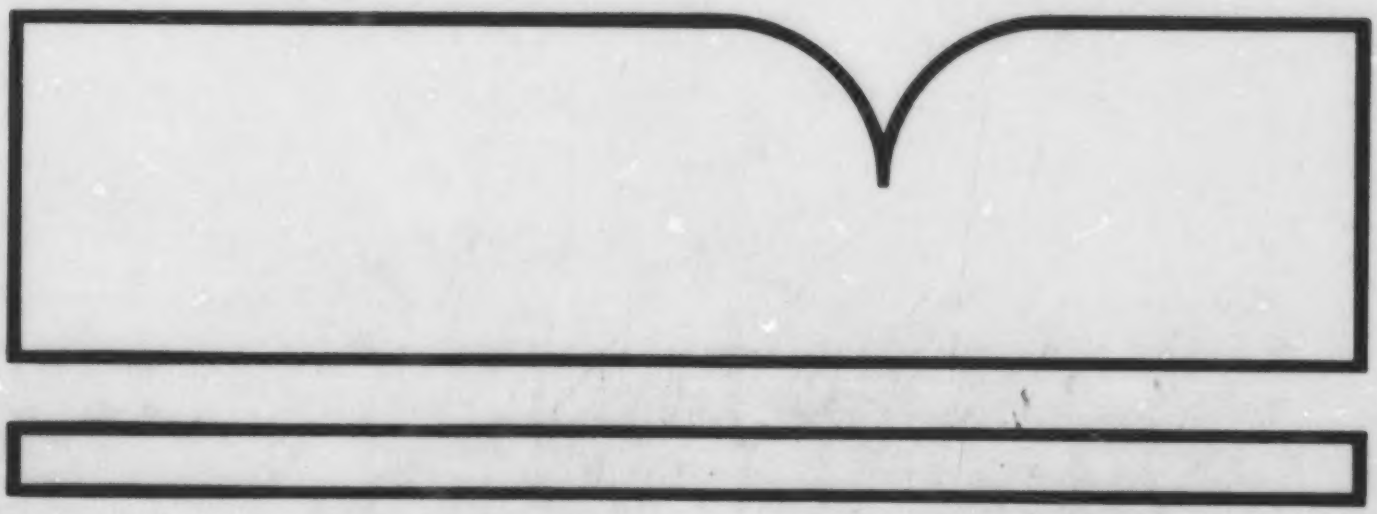

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DEVELOPMENT OF A MULTIDETECTOR PETROLEUM OIL-IN-WATER MONITOR

by

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Contract No. 68-03-2648

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16. ABSTRACT This research report describes an effort to develop a prototype petroleum oil-in-water monitoring system that will continuously measure oil (whether free, suspended, dissolved, or emulsified) in water carrying a variety of potential interfering substances. An extensive desk-top survey of commercially available oil monitors was carried out. Three devices were selected for thorough laboratory evaluation: (1) Sigrist Fluorescence Monitor Model FLJ, (2) CE Invalco D.O.W. Monitor, and (3) Horiba OCMA-25 Oil Content Monitor. The laboratory evaluation of the three oil detectors forms the majority of this report. The work is described in detail, including the construction of a flow loop and its operation, the installation of the selected detectors in the breadboard system, the development of a data retrieval system, the calibration methodology employed, the initial checkout of the detectors, and the extensive multidetector evaluation of each detector's performance for quantifying petroleum oil in the presence of impurities and other interferents. Included is a comprehensive discussion of results and conclusions derived from the data reduction phase of the work. The interferent effect and the sensitivity, linearity and accuracy, repeatability, response speed, and reliability of each detector are described in detail.

Recommendations for a preliminary design for the prototype system and a suggested program plan to develop it are also given.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This research report describes an effort to develop a prototype petroleum oil-in-water monitoring system that will continuously measure oil (whether free, suspended, dissolved, or emulsified) in water carrying a variety of potential interfering substances.

Francis T. Mayo, Director
Municipal Environmental Research
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ABSTRACT

This research report describes the first two phases of an effort to develop a prototype petroleum oil-in-water monitoring system that will continuously measure oil (whether free, suspended, dissolved, or emulsified) in water carrying a variety of potential interfering substances. An extensive desk-top survey of commercially available oil monitors was carried out. Three devices were selected for thorough laboratory evaluation. Recommendations for a preliminary design for the prototype system and a suggested program plan to develop it are also given.

The laboratory evaluation of the three oil detectors forms the majority of this report. The detectors are:

1. Sigrist Fluorescence Monitor Model FLJ

2. CE Invalco D.O.W. Monitor

3. Horiba OCMA-25 Oil Content Monitor

The work is described in detail, including the construction of a flow loop and its operation, the installation of the selected detectors in the breadboard system, the development of a data retrieval system, the calibration methodology employed, the initial checkout of the detectors, and the extensive multidetector evaluation of each detector's performance for quantifying petroleum oil in the presence of impurities and other interferents. Included is a comprehensive discussion of results and conclusions derived from the data reduction phase of the work. The interferent effect and the sensitivity, linearity and accuracy, repeatability, response speed, and reliability of each detector are described in detail.

This report was submitted in partial fulfillment of Contract No. 68-03-2648 by Rockwell International, Environmental Monitoring & Services Center, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1978 to January 1981, and work was completed as of January 15, 1981.

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CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables viii
Acknowledgment ix

1. Introduction and Summary 1
   Background 1
   Objective 2
   Desk-Top Evaluation Study 2
   Experimental Evaluation Study 3
2. Conclusions 4
3. Recommendations 5
4. Experimental System 6
   Flow Loop. 6
      Description 6
      Operation 9
   Detectors 10
      Sigrist 10
      Invalco 12
      Horiba 15
   Data Readout 18
5. Experimental Study 21
   Calibrations 21
      Pump 21
      Rotameters 21
      Detectors 23
   Detector Checkout 28
      Hydrocarbons 28
      Organics 30
      DF-2/KHP 31
   Multidetector Evaluation 33
      Response Data 33
      Results and Discussion 42
6. Suggested Design and Development Work 60
   Preliminary Prototype Design 60
      Flow Loop 60
      Data Retrieval System 61
   Prototype Development Program 63
      Laboratory Testing 63
      Field Testing 64

Appendix: Oil Monitor Survey. 65

FIGURES

Number		Page
1	Flow loop (conceptual design) used in evaluation testing	7
2	Experimental flow loop used for laboratory evaluation.	8
3	Reservoir/rotameter systems used for introducing oils and interferents into eductor subloop	8
4	Selected detectors and associated recorders (on right) used in laboratory evaluation	9
5	Schematic of the Sigrist Fluorescence Meter operation.	11
6	Sigrist Fluorescence Meter Model FLJ with "free fall" flow cell attached.	12
7	Schematic of Invalco D.O.W. Monitor operation.	13
8	Invalco D.O.W. Monitor with sample cell and optical housings visible	14
9	Schematic of Horiba Model OCMA-25 optical system	15
10	Horiba OCMA-25 with sample/solvent internal flow loop visible. .	16
11	Schematic of Horiba OCMA-25 flow loop.	17
12	Portion of a typical Digistrip data readout for a flow test. . .	19
13	Portion of a typical LIC analog readout for a flow test.	20
14	Effect of pressure on main system flowrate	22
15	Effect of R-2-15-AA-SS rotameter setting on flowrate of DF-2 . .	23
16	Horiba control unit pulled forward, exposing circuit board switches	27
17	Effect of water type and temperature on Sigrist response to DF-2	44
18	Effect of water type and temperature on Sigrist response to Gulf crude oil	45

FIGURES (Continued)

Number		Page
19	Effect of time on Sigrist response to Gulf crude oil in fresh tap water at room temperature	47
20	Effect of water type and temperature on Invalco response to DF-2	49
21	Effect of water type and temperature on Invalco response to Gulf crude oil	50
22	Effect of time on Invalco response to Gulf crude oil in fresh tap water at room temperature	52
23	Effect of water type and temperature on Horiba response (without acid injection) to DF-2	54
24	Effect of water type and temperature on Horiba response (with and without acid injection) to Gulf crude oil	55
25	Effect of time and acid injection on Horiba response to Gulf crude oil in fresh tap water at room temperature	57
26	Conceptual flow loop design for prototype system.	61

TABLES

Number		Page
1	Benzene Recovery in Flow Loop Effluent	24
2	Measured Sigrist Reference Cell Relationships (Normalized to FLJ-100)	25
3	Invalco Response to Selected Hydrocarbons	29
4	Detector Responses to Selected Organics	30
5	Detector Responses to DF-2/KHP	32
6	Detector Responses to DF-2 - Run A	35
7	Detector Responses to DF-2 - Run B	35
8	Detector Responses to DF-2 - Run C	36
9	Detector Responses to DF-2 - Run D	36
10	Detector Responses to DF-2 - Run E	37
11	Detector Responses to DF-2 - Run L	37
12	Detector Responses to DF-2 - Run M	38
13	Detector Responses to Gulf Crude Oil - Run F	39
14	Detector Responses to Gulf Crude Oil - Run G	39
15	Detector Responses to Gulf Crude Oil - Run H	40
16	Detector Responses to Gulf Crude Oil - Run I	40
17	Detector Responses to Gulf Crude Oil - Run J	41
18	Detector Responses to Gulf Crude Oil - Run K	41
19	Precision of Sigrist Linear-Curve-Fitted Data	46
20	Precision of Invalco Linear-Curve-Fitted Data	51
21	Precision of Horiba Linear-Curve-Fitted Data	56

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SECTION 1

INTRODUCTION AND SUMMARY

BACKGROUND

The Federal Water Pollution Control Act, as amended, directs the Administrator of the U.S. Environmental Protection Agency (EPA) to establish regulations for the discharge of oil. As a result, the EPA issued Regulations on Discharge of Oil (40CFR110, November 25, 1971), wherein Section 110.3 states that discharges are determined to be harmful that:

(a) Violate applicable water quality standards, or

(b) Cause a film or sheen upon or discoloration of the surface of the water or adjoining shoreline or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

The regulations make it unlawful to discharge oil of any kind or in any form.

Presently, no satisfactory commercially available instrument or concept exists for continuously measuring all types of oil in various physical states -- free, suspended, dissolved, emulsified -- in water containing various types and concentrations of matrix materials. Oil monitors currently available or being developed rely on single detection concepts. Each concept has inherent advantages and disadvantages that may significantly influence the accuracy of results. Factors such as oil type, water characteristics, particulates, and nonpetroleum contaminants all influence the accuracy and may result in errors of a factor of 2 or more.

The complex chemical composition of petroleum-derived oils and the similarities of oil components to nonpetroleum water contaminants dictate the use of a multidetector monitoring system for the improved measurement of petroleum oil in water containing nonpetroleum contaminants. The concept is that a combination of different detectors would be integrated into a viable system that, once calibrated for a particular oil, responds to the various compounds it detects but acknowledges the ratio that is characteristic of the petroleum oil being monitored. Accurate and specific measurements can therefore be performed despite the presence of a limited number of interfering nonpetroleum contaminants by subtracting the contribution of the interfering materials from the total response.

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OBJECTIVE

The ultimate purpose of this study is to minimize the discharge of harmful quantities of petroleum oil into U.S. waters from all sources (including both onshore and offshore facilities, petroleum transport tankers, and other marine cargo vessels) by increasing the qualitative and quantitative detection capability for petroleum oil in water, industrial effluents and other discharges. This capability for detection of petroleum in water will take the form of a multidetector monitoring system. The multidetector system will have the potential for monitoring the level of petroleum oil present in discharge bilgewater from marine cargo vessels and in discharge effluents from offshore oil platforms, oil tankers, and ballast treatment plants. Applications may also include detection of crude oil leaks/seepages into the ocean from drilling operations around and related to marine oil drilling rigs.

DESK-TOP EVALUATION STUDY

To determine the feasibility of developing a multidetector monitoring system for the continuous quantification of petroleum oil in water, Rockwell EMSC conducted a survey of commercially available oil monitors, This study involved a desk-top analysis of currently available oil monitors and an evaluation of their detection concepts, resulting in recommendation of several highest rated off-the-shelf oil monitors for inclusion in a detection system. The Oil Monitor Survey is included in the Appendix.

More than 40 manufacturers were contacted by telephone to identify oil-in-water monitoring devices that might qualify for the analytical evaluation. From the product literature and telecons, devices produced by 13 firms appeared worthy of evaluation. Technical information deemed pertinent to the evaluation of the 13 devices was obtained and tabulated with respect to 25 technical specifications and qualifications. Rating factors were assigned to each particular parameter, and then each device was rated in accordance with criteria established to reflect differences in the various devices.

In addition, a users evaluation of the top-rated devices in each of three different design categories, based on principle of operation, was conducted to provide additional data for the study.

As a result of the oil monitor survey of manufacturers and users, three commercially available oil-in-water monitors, the Sigrist Fluorescence Monitor Model FLJ (UV fluorescence), the CE Invalco D.O.W. Monitor (UV absorbance), and the Horiba OCMA-32A Oil Content Monitor (extraction with IR absorbance) were recommended for incorporation into the multidetector petroleum oil-in-water monitoring system to be evaluated under the experimental study reported herein. These three oil monitoring devices should detect most petroleum oil components, since insoluble petroleum oil components, consisting mainly of paraffins (aliphatic and naphthenic hydrocarbons), can be detected by a device using solvent extraction with IR absorption, whereas soluble components (generally made up of aromatic hydrocarbons and organic compounds) can be determined by devices using ultraviolet absorption and fluorescence.

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EXPERIMENTAL EVALUATION STUDY

The experimental study involves a laboratory evaluation of the three selected oil monitors, with emphasis on each device's performance in the presence of impurities and other interferents. Development of a preliminary design of the sampling and data processing computer systems for a prototype petroleum detection system based on results of the laboratory evaluation is also included.

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SECTION 2

CONCLUSIONS

1. The multidetector concept, that is, the combination of several different detectors integrated into a system that, once calibrated for a specific oil, quantifies that oil, has been demonstrated as a viable technique for the measurement of petroleum oil in water containing nonpetroleum contaminants.

2. A preprototype multidetector system has been assembled and tested with petroleum oil and has resulted in definite improvement over any single commercially available detector, but will require additional research to become truly effective.

3. Oil monitors currently available or being developed rely on single detection concepts and each concept has inherent advantages and disadvantages that may significantly influence the accuracy of the oil concentration as determined by the individual detector. Factors such as oil type, water characteristics, nonpetroleum contaminants, all influence the accuracy.

4. The three selected oil-in-water detectors fail, on an individual basis, to measure up to their reputed ability to quantify petroleum oil in water. Although the devices detect diesel fuel and crude oil, each fails to discriminate, to some extent, when interferents are present.

   a. With respect to overall capabilities, the Sigrist Fluorescence Monitor Model FLJ appears more capable of quantifying petroleum oil in water with interferents present than the other two detectors tested. However, its capabilities are still too limited to do an effective job by itself.

   b. The CE Invalco D.O.W. Monitor does a good job quantifying petroleum oil-in-water without interferents present. In fact, the Invalco responds to most of the chemicals tested on a one-for-one basis, unlike the other two detectors tested. Unfortunately, its inability to discriminate sufficiently is a major drawback to a multidetector petroleum oil-in-water monitoring system.

   c. The Horiba OCMA-25 Oil Content Monitor does a good job quantifying petroleum oil in water with aromatic hydrocarbons present. On average, the Horiba responds on a somewhat less than one-for-one basis to crude oil and aliphatic hydrocarbons, and on a somewhat greater than one-for-one basis to diesel fuel.

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SECTION 3

RECOMMENDATIONS

1. It is recommended that a subsequent effort be undertaken to develop a prototype multidetector petroleum oil-in-water monitoring system that will include the Sigrist Fluorescence Monitor Model FLJ, the Horiba OCMA-25 Oil Content Monitor, and a replacement for the Invalco D.O.W. Monitor. The development effort should include the following items:

a. A limited review of the commercially available detectors (based on the original oil monitor survey [see Appendix]) should be performed to identify a suitable substitute for the Invalco D.O.W. Monitor, which is marginal for inclusion because of its general inability to discriminate between a known oil and various interferents. If this search does identify a suitable substitute, the identified detector should be evaluated experimentally before inclusion in the multidetector system. If the search is unsuccessful and a determination is made to use the Invalco, then the source of the "zero-shift" problem must be found and eradicated.

b. The Sigrist response suppression by aliphatic hydrocarbons should be investigated further so that a satisfactory resolution may be found.

c. The Horiba OCMA-25 should be an original 0-100 ppm range unit or a factory-converted 0-100 ppm range unit.

d. A system flow loop should be constructed according to a proposed design that allows for calibration of the prototype multidetector system as well as representative sampling of the fluid stream for the three detectors.

e. A data retrieval system consisting of a minicomputer and associated software should be integrated into the prototype multidetector system that will reduce the outputs from the three detectors to a concentration value for the petroleum oil in water. A minicomputer considered acceptable for the assignment is the Radio Shack TRS-80, Model III or its equivalent. The software language considered suitable for this application is BASIC.

2. It is further recommended that a follow-on program be conducted to evaluate the prototype multidetector system first in the laboratory and then in full-scale field trials, the latter at the EPA OHMSETT facility.

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SECTION 4

EXPERIMENTAL SYSTEM

Orders were placed for the three commercial oil-in-water detectors to be used in the multidetector petroleum oil-in-water monitoring system. The CE Invalco D.O.W. (Dispersed Oil in Water) Monitor was obtained by bailment, the Sigrist Fluorescence Monitor Model FLJ by modified bailment arrangement, and a Horiba OCMA-25 Oil Content Monitor by lease. The Horiba OCMA-32A, originally recommended for use, was replaced by the OCMA-25 model. The reasons for this change are discussed in Section 5, Multidetector Evaluation, Results and Discussion.

FLOW LOOP

A flow loop was fabricated for the purpose of evaluating the assembled detectors in a breadboard preprototype system configuration. The flow loop was designed to simultaneously distribute a suitable oil-in-water sample to each of the various detectors. The preprototype or breadboard system is thus capable of introducing oil, with and without various other contaminants, into water in such a manner that reproducible and representative oil-in-water dispersions can be provided to the selected monitoring devices for evaluation. The selected instrumentation was assembled at Rockwell EMSC in accordance with the conceptual flow loop design depicted in Figure 1.

Description

The assembled preprototype system flow loop is shown installed in a laboratory fume hood in Figure 2. Two polyethylene-lined, 0.21-m^3 (55-gallon) drums serve as the water reservoir, providing water to a Price HP175 centrifugal pump. The pump circulates the water through a subloop, wherein the water flows through an eductor (D in Figure 1), aspirating oil and, in some cases, an interferent from individual stainless steel containers. The oil/interferent containers and their associated rotameter/metering valve combinations are highlighted in Figure 3. By suitable manipulation of the metering valve associated with each rotameter, the amount of fluid desired is regulated to produce specific concentrations of the fluid in water. While a portion of the water stream is diverted to the three detectors, shown in Figure 4 along with associated readout gear, the remainder is recycled through the oil eductor subloop where it is joined by fresh quantities of water and oil. At the high linear flowrates produced in the flow loop, a steady-state concentration level is rapidly reached. By appropriate adjustment of the detector metering valves and the drain shutoff valve (see Figure 1), the manufacturer-specified sample flowrate to each detector and the desired total system flowrate can be achieved. This is accomplished by monitoring the detector pressure gauges

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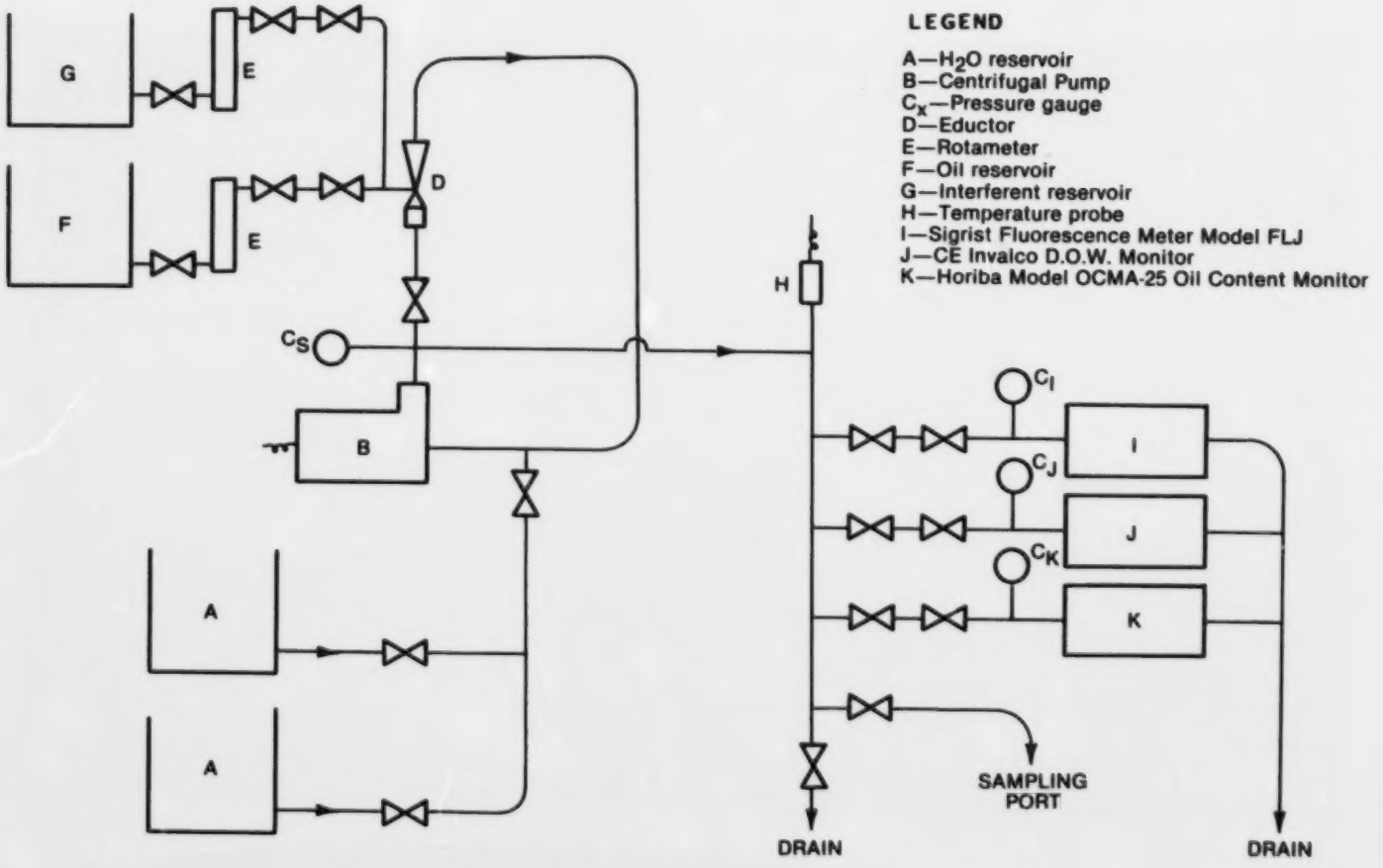

Figure 1. Flow loop (conceptual design) used in evaluation testing.

Figure 2. Experimental flow loop used for laboratory evaluation.

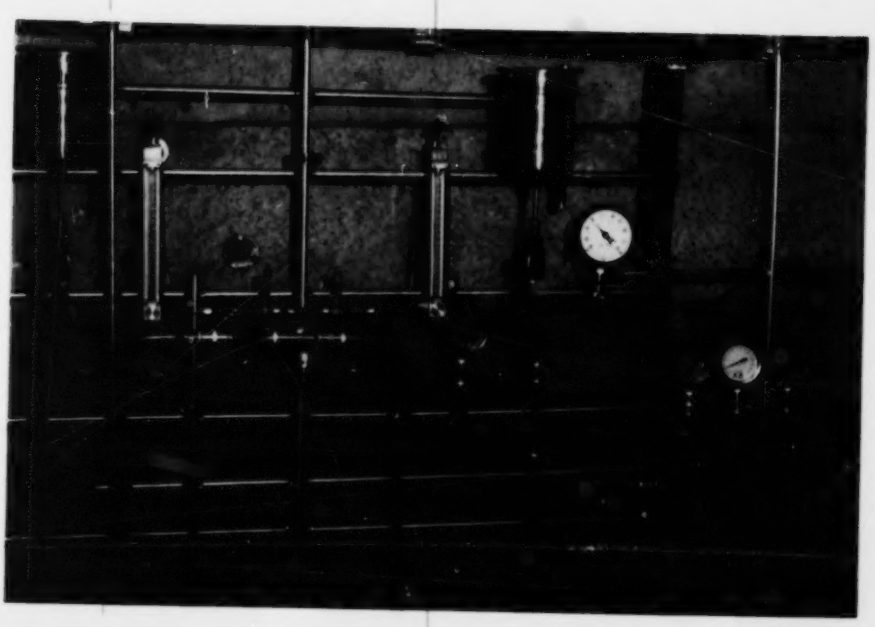

Figure 3. Reservoir/rotameter systems used for introducing oils and interferents into eductor subloop.

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Figure 4. Selected detectors and associated recorders (on right) used in laboratory evaluation.

(C_I, C_J, and C_K) and the system pressure gauge (C_S) for specific pressures that will produce the desired flowrates, as determined from previous flow calibration data. A sampling port is included so that samples can be drawn for analysis to corroborate oil concentrations in water as indicated by preselected rotameter settings.

Also, a Digitec digital thermometer Model 2770A was installed in the flow system for monitoring the temperature of the fluid medium during the course of the laboratory experiments. The thermistor sensing probe is equipped with an integral 1/8-inch NPT fitting and is installed in the flow loop in the vicinity of the detectors.

Operation

In general, a flow run is conducted according to the following procedure. The test matrix is reviewed for desired test parameters, i.e., type and temperature of water, identity and concentrations of known oil, identity and concentration(s) of interferent(s), and so forth. Preparatory experimental steps are taken, such as formulation and thorough mixing of the desired type of water in the 0.21-m^3 (55-gallon) drum(s). Room-temperature tap water can be replenished by a float-valved inlet line, allowing for especially long-duration tests. Other water runs involving sea water or cold/warm water are limited to the volumes prepared in the drum(s). To thoroughly mix the sea water formulation and cold or warm water preparations, the water is circulated through the flow loop and back to the drum(s) by way of a flow line attached to the sampling port. At the same time the oil/interferent reservoir subsystems are emptied of

previous run materials, rinsed thoroughly with appropriate solvents and dried by air-blowing. The desired oil/interferent(s) are then carefully loaded into the respective reservoirs.

To initiate a run the operator opens the detector shutoff valves and the valves leading from the water reservoir. The operator then turns on the centrifugal pump and adjusts the detector metering valves and the drain valve while monitoring the detector flow pressures and the system flow pressure, respectively, so that the proper flow to each detector and the total system outflow will be as desired. When the system pressure is steady (measured by C_5 and set at 3.24×10^5 Pa [32.5 psig], which corresponds to 1.2×10^{-2} m^3 [12 liters/minute]), the shutoff valve to the known oil rotameter is opened and the companion metering valve is adjusted to obtain the desired setting on the calibrated rotameter. When a new setting is desired (not until well after steady state is achieved), the metering valve is adjusted accordingly. If the presence of an interferent is required, a similar procedure is followed with respect to introducing the interferent from the interferent reservoir system. Shortly after initiating flows, the readout system (discussed in this section under Data Readout) is engaged. When steady state, as indicated by the readout system, has been obtained for a given set of flow conditions, the flow conditions can then be modified to produce yet another steady-state readout. In this way, a series of detector readouts is established for a series of oil/interferent concentrations.

To terminate a flow run, the following shutdown sequence is followed: (1) the interferent reservoir shutoff valve is closed, (2) the known oil reservoir shutoff valve is closed, (3) the Horiba is switched to zero water or standby, (4) the centrifugal pump is disengaged, (5) the detector shutoff valves and main water reservoir valves are closed, and (6) the readout recorders are placed in standby mode. Oftentimes the detector responses are monitored and recorded for return to steady-state background following steps 1 and 2.

DETECTORS

The three detectors evaluated during the experimental study were the Sigrist Fluorescence Meter Model FLJ, the CE Invalco D.O.W. Monitor, and the Horiba OCMA-25 Oil Content Monitor. These specific devices were selected on the basis of their reported ability to quantify petroleum oil in water in the presence of various interferents (see Appendix). An important factor in the selection of these three detectors was the consideration that each device should utilize a different principle of operation, thus providing potentially a better defined signature of the known petroleum oil than a group of detectors operating on the same principle. The three devices are further described in the following paragraphs.

Sigrist

The Sigrist Fluorescence Meter is based on the principle that aromatic compounds, present in almost all petroleum oils, have the characteristic, when excited by ultraviolet radiation, of emitting radiation of a higher wavelength than the incident radiation. Through the use of a suitable optical system and

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TYPING GUIDE SHEET

detector, this emitted radiation can be measured and correlated to the concentration of petroleum oil present in a sample.

The operation of the Sigrist Fluorescence Meter is depicted schematically in Figure 5. A mercury (Hg) light source (1) emits a light beam through a calibrated fluorescence comparison standard (6) and a flow cell (5). The measuring beam (3) produced in the flow cell (5) by fluorescent material strikes, together with the light originating from the fluorescence comparison standard (6), the oscillating mirror (2) which alternately emits, about 600 times per second, the measuring beam (3) and a comparison beam (4) onto the photocell (7). The latter, therefore, receives alternately, at identical frequency, a measuring beam (3) and a comparison beam (4) of different light intensity. The photocell (7) transforms the varying intensities of the two light beams into a current, which after subsequent amplification (8) drives a synchronous servomotor (9). This motor, by means of a mechanical shutter (10), regulates the intensity of the comparison beam to such an extent that both light beams directed onto the photocell have an equal intensity. The shutter (10) is coupled mechanically to a measuring drum (11). The indicated value obtained is, therefore, directly dependent upon the position of the shutter. Its position will change only if fluorescence fluctuations influence the intensity of the measuring beam.

The Sigrist Fluorescence Meter Model FLJ, Serial No. 4495, used in the study is shown in Figure 6. The basic unit (on the left) consists of three

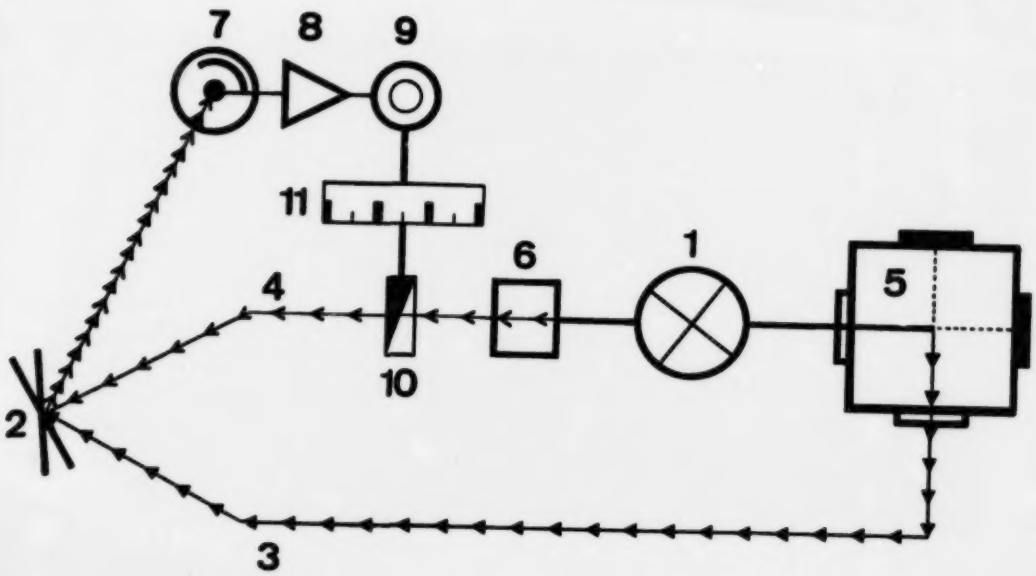

Figure 5. Schematic of the Sigrist Fluorescence Meter operation (reproduced from the Sigrist instruction manual - Fluorescence Meter UP82-FLJ).

Figure 6. Sigrist Fluorescence Meter Model FLJ with "free fall" flow cell attached.

sections: the amplifier assembly at the top, the optical section in the middle, and the recording and transmission section at the bottom. The measurement attachment (on the right) includes the "free fall" windowless flow cell, requiring a sample flowrate of 5-9 x 10^{-3} m^3/minute (5-9 liters/minute), a mercury light source with an average life of 4000 hours, and a portion of the system optics. Together with the basic unit optics, the system is suitable for measurements in the wavelength range of 366 to 2800 nanometers (nm). The manufacturer's representative has indicated that the principal Hg wavelength employed is the 313-nm spectral line. Optical filters are used to accomplish this. The photocell is a secondary electron photomultiplier cell 931 A with built-in rectifier (made by Sigrist-Photometer Ltd). Its spectral range is listed at 366-600 nm, blue-sensitive. The photocell is built into the basic unit, together with the rectifier which provides the excitation voltage. The rectifier produces direct current of 500-900 V which is needed to operate the photocell. The photocell can be replaced like an electronic tube, but a replacement reportedly is rarely necessary.

The function of the fluorescence comparison standards is to produce, in the comparison beam, scattered light of a known intensity (calibrated reference measuring unit), which is then compared with the unknown intensity of the fluorescence light coming from the flow cell.

Invalco

The Invalco D.O.W. Monitor utilizes the principle that clean, clear water will transmit ultraviolet light with very low absorption while most petroleum oils and their derivatives will partially or completely absorb the ultraviolet

light. This is due to the aromatic compounds present in petroleum oils. Variations in absorption of ultraviolet (UV) light by the carrier stream provides a measurement of aromatic content, to which oil content may be related.

The operation of the Invalco D.O.W. Monitor is depicted schematically in Figure 7. While flowing through the sample cell, the sample is continuously monitored by the filtered UV and visible light. The visible light maintains a background reference for the detector circuit. When any contaminant enters the chamber, the UV light is absorbed to a corresponding degree and the measuring cell, a photodiode tube, senses the reduction in the radiant light and produces a corresponding current output. This current is then converted to a voltage that is amplified by the cell amplifier. At the same time the reference photodiode tube senses the filtered visible light and produces a current output that is converted to a voltage and amplified by the reference amplifier. The logarithms of these two voltages are taken and then subtracted. This yields a ratio output signal that should be linearly proportional to oil concentration in the sample stream.

The subtractor/differential amplifier provides an input to the meter/recorder circuit and the 4-20 ma analog conditioning circuit. Consequently, when there are no contaminants or no UV light being absorbed in the measuring cell, the outputs of the two amplifiers will be equal, the output of the differential amplifier zero, the meter indicating zero and an analog output of 4 ma.

The Invalco D.O.W. Monitor, Serial No. Y-171, used in the study is shown in Figure 8. The measuring chamber is located in the middle (with the D.O.W. MONITOR label on it) and is composed of an anodized aluminum block, a quartz glass cell, stainless steel end-caps, neoprene end-cap seals, and mechanical wiper, chamber drain and light filters. The aluminum cell block contains a light port that extends through the block from side to side. The port transmits the UV light from the source (on the left) through the quartz glass sample cell to the photodiode (PD) detector tubes (on the right). The glass sample cell is made of clear fused quartz. Fused quartz is one of the best known

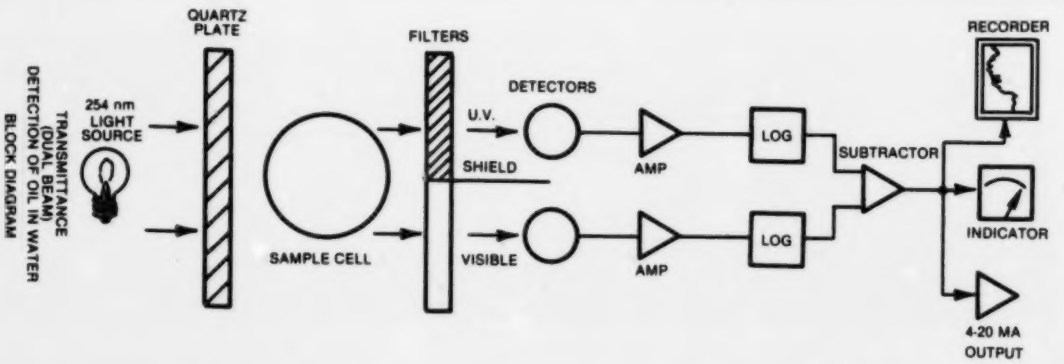

Figure 7. Schematic of Invalco D.O.W. Monitor operation.
(reproduced from the Invalco instruction manual - D.O.W. Monitor)

Figure 8. Invalco D.O.W. Monitor with sample cell and optical housings visible.

transmitters of UV light available. The shortwave cutoff for fused quartz is in the ultraviolet range from 155 to 175 nanometers depending on the fusing procedure used in making the material. This cutoff wavelength is below the minimum of 253.7 nanometers required when the shortwave lamp is used.

The Invalco D.O.W. Monitor optical cell is cleaned at a predetermined interval by an automatic wiper that is intended to reduce contamination of the measuring cell, hence improving the accuracy of the determination. The cleaning cycle is also initiated manually or automatically when the indicating meter rises above the lower limit set point. The instrument has standard local indication with isolated DPDT "Caution" and "High" level contacts for alarms. Also, according to the manufacturer, the device fails safe by indicating "High" oil upon ultraviolet light source failure, excessive inorganic turbidity, or excessive fouling of the optics.

The main components comprising the optical system are the UV light source, UV light source heater, calibration shutter, light filters, quartz glass cell, photodiode detector and reference tubes and the cell wiper. The standard UV light source is a 4-watt shortwave mercury vapor fluorescent lamp that emits approximately 95% UV light in the 254-nanometer peak range and approximately 5% light in the visible region of the spectrum (white light). The expected lifetime of the standard UV lamps is 5000 hours.

To prevent the variation of UV light intensity with temperature change, the device incorporates a semicircular UV light source tube wall heater. This heater is controlled by a solid-state proportional temperature controller that maintains the desired tube wall temperature to within ±0.3°C (0.5°F).

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EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN, EPA FORM 287)
TYPING GUIDE SHEET

The vacuum PD tube is a simple, yet efficient photodetector. The PD tube used in the Invalco Monitor is RCA's 934, chosen for its stability, linearity of photocurrent with radiant light, and spectral response in the UV light range.

Horiba

Solvent extraction/nondispersive infrared absorption is employed in the Horiba Model OCMA-25. Basically, the oil in the sample water is extracted in a solvent, the absorption of which is measured at the wavelength region of 3.4 to 3.5 micrometers by a nondispersive infrared analyzer, and the reading is converted into an equivalent value of oil. The extraction solvent is identified as fluorochlorocarbon solvent S-316*, which, according to the manufacturer, has no infrared absorption in the wavelength region of 3.4 to 3.5 micrometers, extracts oil easily, and has no toxicity.

The optical system utilized in the OCMA-25 is depicted schematically in Figure 9 and the principle of nondispersive infrared absorption as employed in the OCMA-25 is discussed in the following paragraph.

Infrared radiation from matched light sources, converted into an intermittent light beam by a rotating chopper, enters a reference cell and a sample

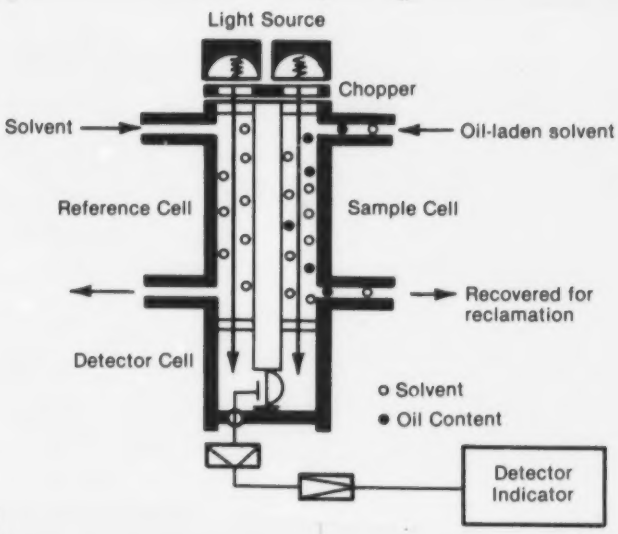

Figure 9. Schematic of Horiba Model OCMA-25 optical system. (reproduced from the instruction manual for Horiba Model OCMA-25 Oil Content Monitor)

* Trademark registered by Horiba, Ltd., Kyoto, Japan.

cell, passing alternately through each of the cells to a detector cell. If any of the infrared radiation entering the sample cell is absorbed by oil in the solvent, it creates a difference in the amount of light alternately reaching the detector cell. Because the detector is filled with a gas that absorbs radiation in the infrared region required for detection of oil content, a thin membrane provided in the detector cell flexes with the resultant change in pressure and an electrical signal corresponding to the difference in the amount of light absorbed is developed. This electrical signal is thus proportional to the oil content of the sample water.

A view of the internal flow loop of the OCMA-25, Serial No. 47618J, used in the study is shown in Figure 10, while the operation of the OCMA-25 is best described by means of the flow schematic depicted in Figure 11. The sample is drawn into the instrument through a strainer by a dual pump, P-1, and then fed to an extractor after a pH adjustment. At the same time, by way of the other head of the dual pump, P-1, the solvent is passed through a reclaimer where oil in the solvent is removed by an adsorbent and, after passing through the reference cell in the infrared analyzer, the solvent is fed into the extractor. By this solvent recycling arrangement, any remaining traces of oil that may be contained in the solvent prior to the extraction can be corrected for during the infrared analyzer measurement. The solvent and the sample are introduced into the extractor in a fixed flowrate ratio by virtue of the dual pump module, and are vigorously mixed by a stirrer revolving at high speed so that the oil in the water will be properly extracted in the solvent.

After the extraction, sample and solvent are separated by a water filter. The oil-laden solvent, after passing through a temperature controller, is fed

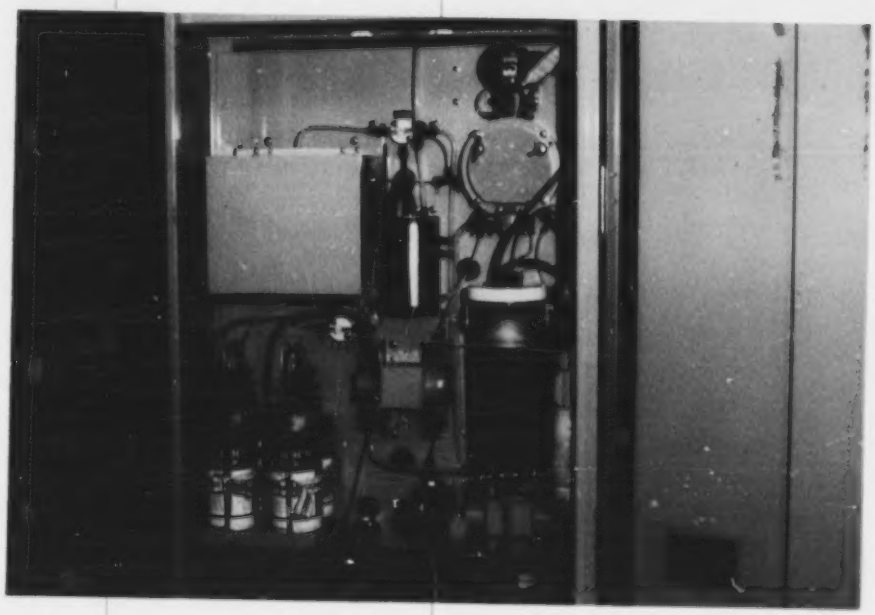

Figure 10. Horiba OCMA-25 with sample/solvent internal flow loop visible.

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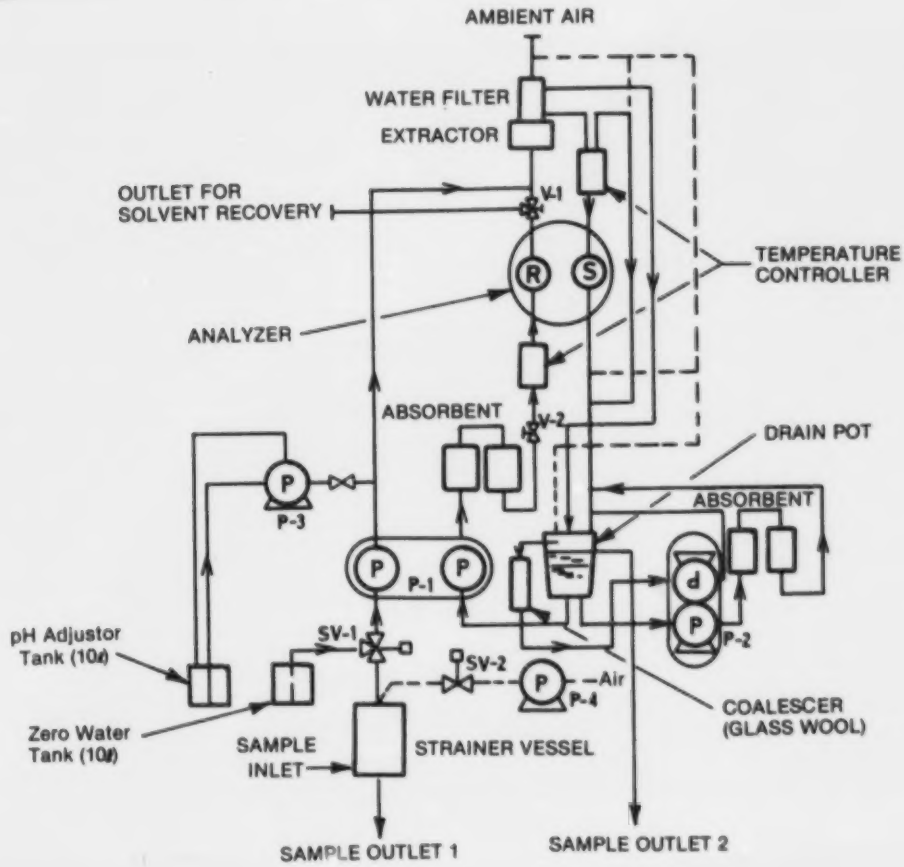

Figure 11. Schematic of Horiba OCMA-25 flow loop. (reproduced from the instruction manual for Horiba Model OCMA-25 Oil Content Monitor)

into the sample cell of the infrared analyzer, and the separated sample water goes to a waste tank (drain pot) after passing through a coalescer element. From the analyzer the oil-loaded solvent is also fed to the drain pot. There the solvent and the waste sample water are separated. The sample water is discharged outside the instrument and the solvent is recycled for subsequent measurements.

A 3-way solenoid valve is provided between the strainer and the pump. It switches from sample water to zero water contained in a 10-liter tank, to calibrate the zero point of the instrument during the calibration procedure. This 3-way solenoid valve is also switched to zero water to stop the introduction of sample water if the oil content exceeds the measuring range of the instrument. This prevents the instrument from being unduly contaminated and extends the serviceable life of the adsorbent.

DATA READOUT

Both the Sigrist and Invalco detectors are equipped with small recorders and the resultant traces provide, perhaps, adequate recorded readouts to indicate general response levels while, at the same time, fulfilling certain legal requirements. The built-in recorders were found inadequate, though, for the evaluative study planned for this program. The Horiba monitor includes a digital response readout but no built-in recorder. As a result, a single-channel Universal Monitoring Corp. (UMC) strip-chart recorder, Model 161, was interfaced with the Invalco D.O.W. Monitor initially. The electrical hookup with the Invalco 4-20 ma current output was accomplished with a 0.10-m (4-inch) length of 30 AWG copper wire used as a current shunt to develop the recorder signal voltage.

When the Sigrist detector was received and a remote readout installed in it, the response outputs from both the Invalco and the Sigrist devices were interfaced with a Linear Instruments Corp. (LIC) dual-channel, strip-chart recorder, Model 485. The electrical interface with both 4-20 ma outputs was accomplished in a similar fashion to that employed with the UMC recorder used earlier.

The final data retrieval system, configured after arrival and installation of the Horiba, included a Digistrip 15-channel digital recorder along with the LIC two-pen recorder. Both recorders can be seen in Figure 4 on the right, with the LIC on top of the Digistrip. An example of a portion of a Digistrip record of a flow test showing a typical set of data from which values were selected for tabulation is depicted in Figure 12. The channel code is as follows:

Channel	Output
H/m	Time in 24-hour format
T	Temperature in °C (0.010 v = 1°C)
H	Horiba response output (1.000 v = 80 ppm)
S	Sigrist response output (1.000 v = 100% FS)
I	Invalco response output (1.000 v = 100% FS)
I_{UV}	Invalco UV detector output (in v)
I_v	Invalco visible detector output (in v)

Because of the response lag of the Horiba (1-1/4 minutes in the original pump module configuration and 2-1/2 minutes in the modified configuration [refer ahead to Section 5, Calibrations, Detectors]), corresponding data for the Horiba would be typically obtained 2-1/2 minutes later than the real-time data for the Sigrist or Invalco.

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H/m	T	H	S	I	I_{UV}	I_V
12 05	0.177	0.798	0.592	0.492	0.306	0.474
12 06	0.177	0.774	0.572	0.465	0.314	0.479
12 06	0.177	0.724	0.585	0.483	0.311	0.476
12 06	0.177	0.676	0.484	0.500	0.309	0.479
1 12 06[2]	0.177[3]	0.641[4]	0.635[5]	0.495[6]	0.301[7]	0.471[8]
12 07	0.177	0.616	0.580	0.485	0.304	0.474
12 07	0.177	0.607	0.598	0.487	0.305	0.473
12 07	0.177	0.600	0.502	0.497	0.310	0.478
12 07	0.177	0.593	0.537	0.513	0.306	0.471
12 08	0.177	0.594	0.576	0.445	0.319	0.482
12 08	0.177	0.589	0.555	0.555	0.290	0.471
12 08	0.177	0.585	0.631	0.494	0.304	0.472
12 08	0.177	0.586	0.533	0.505	0.305	0.477
12 09	0.177	0.582	0.520	0.428	0.330	0.487
12 09	0.177	0.578	0.496	0.493	0.315	0.481
12 09	0.177	0.579	0.607	0.480	0.306	0.472
1 12 09[2]	0.177[3]	0.578[4]	0.552[5]	0.462[6]	0.313[7]	0.468[8]
12 10	0.177	0.576	0.578	0.483	0.312	0.476
12 10	0.177	0.573	0.621	0.471	0.306	0.469
12 10	0.177	0.569	0.576	0.478	0.308	0.474
12 10	0.177	0.567	0.576	0.558	0.293	0.471
12 11	0.177	0.572	0.391	0.395	0.348	0.492
12 11	0.177	0.573	0.477	0.431	0.331	0.488
12 11	0.177	0.571	0.099	0.242	0.425	0.553
12 11	0.177	0.569	0.116	0.208	0.437	0.555
12 12	0.177	0.565	0.071	0.206	0.442	0.559
12 12	0.177	0.562	0.061	0.217	0.438	0.559
12 12	0.177	0.562	0.036	0.189	0.453	0.565
1 12 12[2]	0.177[3]	0.557[4]	0.032[5]	0.189[6]	0.454[7]	0.567[8]

Figure 12. Portion of a typical Digistrip data readout for a flow test. (Except for the time channel, readouts are in volts.)

The LIC two-pen strip-chart recorder, wired to the output of the Sigrist and Invalco units to provide a real-time analog display of response data, continued in use, providing valuable diagnostic data on the performance of the flow loop as well as the detectors. A portion of a typical strip-chart record of a flow test with the response traces for the Sigrist and Invalco identified is depicted in Figure 13. Zero to 100% FS for the detectors is zero to full scale on the chart paper, with zero on the left. Any perturbations observed in the traces have been attributed principally to the flow loop and, except for minor oscillations present in the Sigrist trace, are not due to detector characteristics. The baseline difference is due to the sample stream background as perceived by each device.

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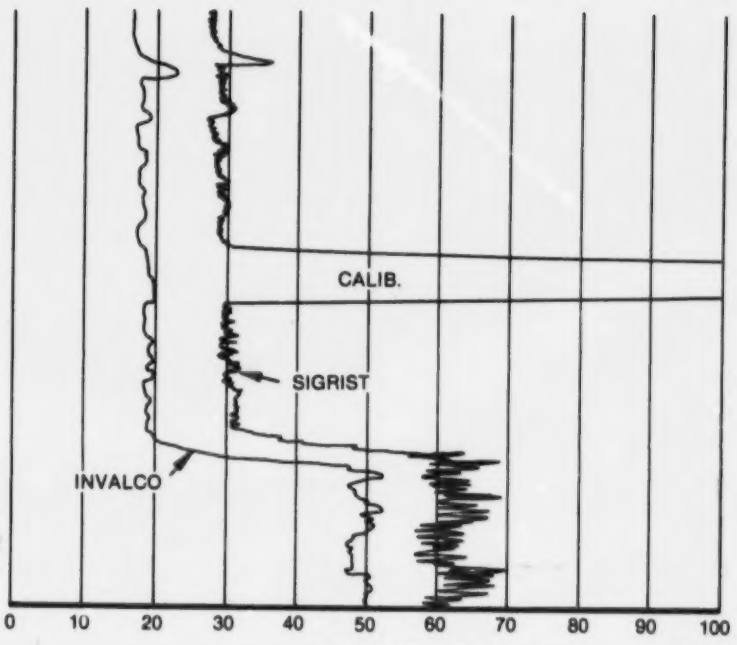

Figure 13. Portion of a typical LIC analog readout for a flow test.

SECTION 5

EXPERIMENTAL STUDY

Following successful operation of the laboratory flow loop with tap water, various calibration and checkout tests were performed before conducting the multidetector evaluation tests.

CALIBRATIONS

Before flow testing of the detectors could begin in earnest, certain calibration data were required. Data on the centrifugal pump flowrates with pressure and on rotameter flowrates with various fluids were obtained by measurements conducted in the laboratory. In addition, certain other calibration checks specific to the selected detectors were performed.

Pump

Centrifugal pump flowrates were measured at several flow loop pressures and a flow curve was developed from the data. During flow tests, the Price centrifugal pump thermal overload protection switch repeatedly disengaged the pump after 10 to 15 minutes of continuous operation. To correct the problem, the pump was returned to the supplier, who completely rebuilt the pump (under warranty) by replacing the impeller and upgrading the pump motor (from 1 to 1.5 HP). The pump was reinstalled in the system and flow tests indicated the problem had been corrected. A subsequent flow curve was developed and it confirmed the previous flow curve and is shown in Figure 14.

Rotameters

The primary method for determining the concentration levels of various fluids used either as known oils or interferents involved the use of laboratory-calibrated rotameters (E in Figure 1) in the flow loop. Verification was obtained from subsequent analytical determinations.

Description--

The rotameters were manufactured by the Brooks Instrument Division of Emerson Electric and are of the Sho-Rate "150" type employing a 0-150 mm etched scale, ten-to-one rangeability, and completely interchangeable tubes and floats. The floats consisted of either glass, sapphire, or stainless steel spheres and the tube designations (Brooks) were R-2-15-AAA, R-2-15-AA, and R-2-15-D. Except for a few cases where only a crude indication of flowrate was required, such as in some of the detector checkout tests, rotameter tube/float combinations selected for a specific fluid were calibrated with that fluid under controlled conditions at room temperature. For example, an

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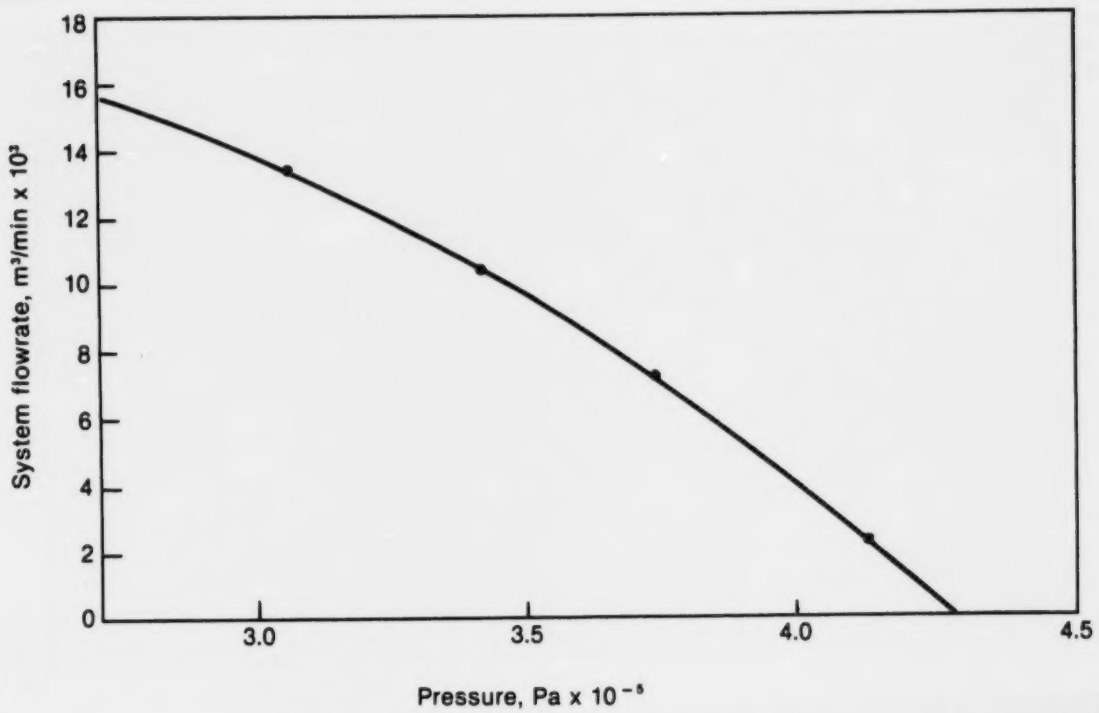

Figure 14. Effect of pressure on main system flowrate.

R-2-15-AA rotameter with a stainless steel float, intended to be used for flow tests with diesel fuel (DF-2), was calibrated by flowing DF-2 through it at four different steady-state float settings. The DF-2 passed during a measured time period at each setting was caught in a graduated cylinder and its volume determined. Data from such a run were used to produce the calibration curve that appears in Figure 15. Rotameters used in the development of detector checkout data and multidetector evaluation data are identified in the respective data tables. However, as noted above, during the detector checkout study some rotameters were used for indication purposes only.

Verification--

To verify the technique of employing laboratory-calibrated rotameters for determining the concentrations in water of various oils and interferents being introduced into the flow loop, a flow run was conducted with tap water at room temperature into which reagent-grade benzene was introduced by a calibrated rotameter. (The rotameter used was a Brooks R-2-15-AA with a stainless steel spherical float.) Duplicate effluent samples at three concentrations were drawn from the flow loop at the sampling port (see Figure 1) and analyzed by gas chromatography (GC). The analytical instrumentation involved a Perkin Elmer Model 3920, with an OV17 column and an FID detector, and a Hewlett-Packard HP3380A integrator.

A calibration curve was developed using standards of benzene in water

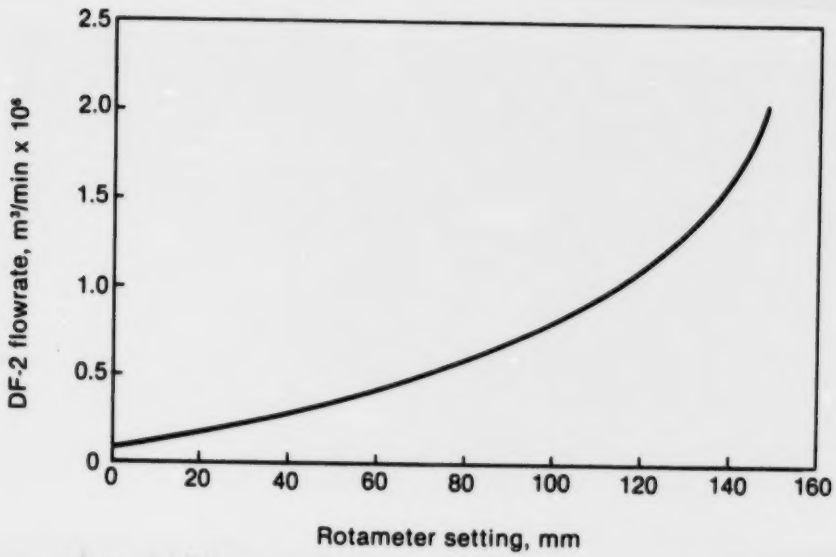

Figure 15. Effect of R-2-15-AA-SS rotameter setting on flowrate of DF-2.

prepared by injecting a known quantity of benzene (using a microliter syringe) into 9 x 10^{-4} m^3 (900 ml) of deionized water in a glass bottle, the contents of which were then stirred using a magnetic stirrer. The contents were transferred to a separatory funnel, wherein the benzene was extracted with carbon disulfide, CS_2. A portion of the CS_2 was collected in a Mininert vial, from which samples were drawn for the GC measurements. The effluent samples, also of a volume of 9 x 10^{-4} m^3 (900 ml), were treated in the same fashion, excluding the stirring step.

Results of the analytical determinations on the benzene flow loop effluent appear in Table 1. Considering the volatility of benzene and the losses that may occur during effluent sampling, the average recovery percentages are quite reasonable and indicate that the loss of benzene in the flow loop is minimal, thus confirming the validity of using laboratory-calibrated rotameters for determining the oil/interferent concentration levels in water.

Detectors

Various calibration methodology are described by the manufacturers in their respective manuals for the detectors. Manufacturer-specified calibration methods such as the Invalco Monitor procedure using a series of known oil aliquots in benzene measured independently with a Bausch & Lomb Spectronic 20 spectrophotometer were deemed not necessary for inclusion in the multi-detector calibration methodology. In fact, the diversity of the principles of operation employed in the three detectors predetermined that a real-time quantification of the oil-in-water dispersions be established by such a technique as that using calibrated rotameters. On the other hand, certain other device-specific, built-in calibration functions were deemed appropriate to use during this study and, therefore, are discussed in the subsequent paragraphs.

TABLE 1. BENZENE RECOVERY IN FLOW LOOP EFFLUENT*

Rotameter Concentration (ppm)	Analytical Concentration (ppm ±1 SD)	Recovery Average (%)
55	46.2 ±0.8	85
55	46.7 ±0.4	
91	82.8 ±0.4	87
91	75.5 ±1.5	
110	97.8 ±1.1	89
110	98.3 ±1.1	

* The effluent from a flow test using reagent-grade benzene was retrieved at the flow loop sampling port and was analyzed by gas chromatography.

Sigrist--

The reference cells, alluded to in Section 4, Detectors, Sigrist, are used in the optical beam path of the Sigrist Fluorescence Meter to provide a calibrated reference standard against which the sample can be compared. Four reference cells were provided with the FLJ flow cell (three of which are seen on top of the right-hand measuring attachment in Figure 6). Their manufacturer designations are FLJ5, FLJ10, FLJ20, and FLJ100. The last figure of each designation refers to the measuring range in ppm of quinine sulfate, the standard against which they were calibrated by the manufacturer.

A reference cell is installed by opening the small door in the measuring attachment (on the right side in Figure 6) and sliding the comparison standard through the small door and pushing it to the rear. The instrument is adjusted to 100% FS after every change of the comparison standard. The operator should be sure that the small door of the measuring attachment is locked when adjusting to 100% or when measurements are taken. This will prevent outside light from getting into the optical system, and influencing the measurements.

To adjust the double beam system to 100%, the lever underneath the measuring attachment is set to "100% Adjustment." This causes a deflector to direct the comparison beam coming from the fluorescence comparison standard to the basic unit. Fine adjustment to 100% is made by turning the adjustment knob on the front panel of the basic unit. The diaphragm controlled by the adjustment knob is able to influence the light intensity of the measuring beam on the order of about 40%.

Results of response measurements of the Sigrist device to several fluids for each of the reference cells are shown in Table 2. The average measured response (normalized to FLJ-100) is in fairly good agreement with the theoretical ratios (also listed).

TABLE 2. MEASURED SIGRIST REFERENCE CELL RELATIONSHIPS (NORMALIZED TO FLJ-100)

Fluid Medium	FLJ-5	FLJ-10	FLJ-20	FLJ-100
Tap water	20	7.3	3.3	1.0
Quinine sulfate in deionized water	S	8.3	3.3	1.0
Diesel Fuel 2 (DF-2) in tap water	S	12.4	5.4	1.0
Average measured response	20	9.3	4.0	1.0
Theoretical response	20	10	5	1

S = saturated.

The solution of quinine sulfate in deionized water was prepared and pumped through the Sigrist flow cell in an attempt to verify the manufacturer's absolute calibration of the reference cells. However, the quinine sulfate sample obtained for the formulation was not pure, having been adulterated with an excipient, such as milk sugar, by the manufacturer/supplier. As a result, when the Sigrist response to the quinine sulfate solution was found to be significantly higher than the calculated value, corrected for the stipulated adulteration, the data became suspect and unworthy of use in an absolute calibration of the reference cells. Nevertheless, the quinine sulfate solution was still useful in verifying the relative values of the reference cells, as seen in Table 2. This inability to produce an absolute calibration of the Sigrist reference cells was not considered serious, since laboratory-calibrated rotameters were to be the primary standard for determining the concentrations of various fluids (see this section, Calibrations, Rotameters).

Invalco--

The instrument indicates oil content as percent absorption which is converted to parts per million (ppm) by means of other absolute total oil content determination. The detection range for crude, fuel and lube oils is normally 0-150 ppm of "dispersed" oil in water relative to the oil being monitored. Accuracy is described as ±5% oil content throughout the full range of the instrument.

According to the calibration section of the instruction manual, a meter and an analog output calibration are described. For purposes of brevity, the latter is discussed here. Although the procedures call for the power to be applied for 24 hours prior to calibration with the process stream flowing through the unit, this is not always feasible nor does a flowing stream of tap water prevent a zero background shift. Once the meter calibration is performed, the next step is to calibrate the analog output. With the external circuitry properly connected to the Invalco terminal strip, the panel-mounted

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Operate/Calibrate switch is moved to the calibrate position and the cell wiper is run two or three times to remove any free oil or air bubbles from the cell wall. Using a volt-ohmmeter, the analog zero potentiometer is set for 4 ma output. The shutter switch (seen in Figure 8 in the front panel of the light source module on the left) is then held in the shutter position for no more than 1 minute while the analog span potentiometer is set for 20 ma output. (Certain types of acrylic plastic exhibit the ability to restrict the transmission of ultraviolet light. To provide a means of calibrating the Invalco Monitor for a meter reading of 100% absorption, an acrylic plastic shutter is incorporated in the optical system. This plastic shutter, which restricts a large portion of the transmitted UV light, sets an arbitrary but repeatable 100% absorption point on the meter when placed between the UV source and the measuring cell PD tube. The shutter is operated during calibration by means of a rotary solenoid. The solenoid is an intermittent-duty device and should not be held in the energized position for a period longer than 1 minute.) If necessary, again adjust the zero potentiometer output for 4 ma, then return the Operate/Calibrate switch to the Operate position.

The meter and analog calibrations as well as a "shop calibration procedure" described in the manual were faithfully performed until the zero shift (alluded to before) became too great to compensate for by the adjustment. A discussion of this "zero-shift" problem can be found in Section 5, Multidetector Evaluation, Results and Discussion.

Horiba--

"Oil content," as measured by the OCMA-25 and defined by the manufacturer, is "the compounds extracted into fluorochlorocarbon solvent S-316* which show infrared absorptions in a wavelength range of 3.4 to 3.5 micrometers converted in terms of the concentration (V/V) of a calibrating oil (B-heavy oil)."** Calibration of the instrument is done by standard solutions of B-heavy oil prepared at the time of calibration.

After installation the instrument should be run for 2 to 3 hours with the calibration selection switch (CSS) set at "ZERO" and the MEAS/STANDBY (M/S) switch at the "MEAS" position, thus drawing zero water into the device. The M/S switch is then set at "STANDBY." The control unit, CU, is pulled forward on its track, as shown in Figure 16, and the "CHECK" switch of the MEAS/CHECK/ADJUST switches on the printed circuit board is depressed. A clean 200-ml flask is placed in position for collecting solvent from the solvent-dispensing valve (V-1 in Figure 11) and the M/S switch is set at "MEAS" until 200 ml of solvent is collected, whereupon the valve is returned to its original position. The collected solvent is next drawn into a Teflon tube in the sample inlet line by pushing the "OFF" position of the CSS. When the measured response has stabilized, the ZERO control in the CU is adjusted to indicate zero. The M/S switch is set at "STANDBY." Again, 200 ml of solvent is drawn from the system (using the procedure described previously) but now the volume is accurately

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* Trademark registered by Horiba, Ltd., Kyoto, Japan.

** Instruction Manual for Horiba Model OCMA-25 Oil Content Monitor, Horiba, Ltd., Kyoto, Japan.

Figure 16. Horiba control unit pulled forward, exposing circuit board switches.

measured into a volumetric flask to which 9.6 microliters of B-heavy oil is added. The concentration of the standard solution is 48 ppm (by volume) and when introduced into the sample inlet line (by the same technique used before) the indicated readout should be adjusted to 16 ppm by way of the SPAN control in the CU.

With the pump module (P-1 in Figure 11) in its original alignment, the sample-to-solvent volume flow ratio is 2:1. Thus, a 48-ppm dispersion of oil in solvent will be diluted to 32 ppm when mixed with pure solvent in the ratio of 2:1. In a situation where a 48-ppm dispersion of oil in water is drawn into the sample inlet line and mixed with extracting solvent, the oil would be concentrated in the extracting solvent by a factor of 2. Therefore, to provide for a direct readout in ppm oil-in-water, the 32-ppm reading should be divided by 2, giving 16 ppm. Note: When the pump module, P-1, was reversed (to extend the range of the OCMA-25), the internal sample-to-solvent ratio became 1:2. Applying the same reasoning with the new configuration means that the span-control-adjusted reading should be 32 ppm. However, because the SPAN control could only be adjusted to a readout of 8 ppm, rather than the calculated 32, all direct instrument readings have to be multiplied by 4. (It should be noted that Digistrip readings in volts have to be multiplied by 80 to convert to ppm.)

Following the above calibration procedure with the pump module in its original configuration, the unit was calibrated using B-heavy oil, Lot #M9N7694, and fluorochlorocarbon solvent, Lot #00313. Other reference solutions formulated with the same solvent and introduced in the same manner for comparison with the B-heavy oil calibration at 16.0 ppm_v resulted in the following ppm_v

readouts: DF-2, 16.3; isooctane, 14.3; and benzene, 0.1.

In addition to the above-described calibration steps (which the manufacturer suggests be performed once a month) the OCMA-25 has an automatic calibration feature that allows the device to adjust zero and span at regular programmable intervals or at operator behest if so desired. The autocal procedure takes approximately 20 minutes.

DETECTOR CHECKOUT

The oily water flow loop was first engaged with the Sigrist FLJ Fluorescence Meter and the CE Invalco D.O.W. Monitor in operation. The reason for lack of inclusion of the Horiba OCMA-25 in these checkout tests was the manufacturer's delay in delivery of the device. If the Horiba had been delivered earlier than it was, some of these tests would have been conducted on the preprototype multidetector system and would thus have qualified for inclusion under this section, Multidetector Evaluation. Initial trial runs were designed to familiarize the operator with the flow system and its operational characteristics as well as the detectors and their characteristics.

Hydrocarbons

Dispersions of selected hydrocarbons in water were produced by aspirating the hydrocarbon through the eductor into the flow stream at precalculated rotameter float settings based on a fixed tap-water flow in excess of that demanded by the two devices. The desired system pressure was achieved by diverting the excess water mixture into a disposal network. Trials with the Sigrist and Invalco devices were conducted with room-temperature water at flowrates of approximately 5 and 2 liters/min, respectively. The results are listed in Table 3. Rotameter settings during these trial runs were used for indication purposes only. A Brooks R-2-15-AA-SS rotameter was used for introducing each of the hydrocarbons, and the FLJ-5 reference cell was used in the Sigrist.

Several observations can be made from the preliminary data found in Table 3. First, lower-boiling aromatic hydrocarbons, such as benzene and o-xylene, produce essentially minimal responses (less than 0.1 ppm) in the Sigrist device. The Sigrist ignores them much the same as it does aliphatic hydrocarbons. The reason for this is believed to be the manufacturer's optimization of the device for crude oils, that is, the light source/detector combination may be more suited for detection of fluorescence from higher aromatics.

A second observation is that the Invalco unexpectedly responds to aliphatic as well as aromatic hydrocarbons. This behavior of the Invalco device, that is, its inability to distinguish between aliphatic and aromatic hydrocarbons, suggests that the device may be extremely sensitive to turbidity. Although this behavior may be tolerated on an individual detector basis provided the response, potentially a product of UV absorbance and scatter, is reproducible for a specific concentration of a known oil, it portends a serious deficiency for a multidetector system that intends to utilize the discriminating abilities of several detectors to distinguish between a known oil and one or more interferents. Also, the Invalco response may be affected by varying amounts and/or types of interferents since the attenuation of light is

TABLE 3. INVALCO RESPONSE TO SELECTED HYDROCARBONS*

Hydrocarbon	Rotameter Setting≠ (mm)	Response Conc (ppm)	Hydrocarbon	Rotameter Setting≠ (mm)	Response Conc (ppm)
Benzene	15	60	Isooctane	150	78
	38	120		100	45
	50	141		50	23
	50	150		38	20
	50	145		15	12
Isooctane	150	68			
	150	66	Benzene	150	S
				100	167
Benzene	50	156		50	140
	38	140		38	123
	15	77		15	33
	50	146			
	38	132			
Dodecane	150	54	o-xylene	150	S
				100	168
Nonane	150	63		50	99
				38	78
n-octane	150	71		15	38

* Although the Sigrist Fluorescence Meter was actively engaged in these runs, none of the listed hydrocarbons produced more than a negligible (less than 0.1 ppm) change from the Sigrist background response with an FLJ-5 reference cell in the Sigrist.

≠ A Brooks R-2-15-AA-SS rotameter was used throughout the runs to introduce the various hydrocarbons into the flow stream. It was used for indication purposes only.

S = Saturated.

dependent on particle size as well as concentration.

Additional observations can be made by viewing the benzene data. These data suggest that the Invalco response or measured concentration is relatively repeatable with respect to the concentration (as indicated by the rotameter setting), although the data do exhibit a deteriorating bias in Invalco sensitivity with time, perhaps requiring a regularly scheduled calibration for field applications.

Organics

Preparatory to studying the effect of organics, as interferents, on the measurement of petroleum oils in water, the responses of the Sigrist and Invalco devices to a number of organics in room-temperature tap water were determined. The runs were conducted using an R-2-15-AA-SS rotameter for each of the fluids and the FLJ-5 reference cell in the Sigrist. The data are listed in Table 4. Concentration values were calculated from rotameter settings and a water calibration curve; the methanol rotameter setting was used for indication purposes only.

A number of observations can be made from the data in Table 4. First, as expected, the Invalco does not respond to methanol, a nonaromatic water-soluble compound, adding further credence to the belief that the Invalco senses other nonaromatics because they are essentially insoluble in water and, thereby, scatter UV radiation rather than absorb it. It should be noted that the turbidity of a number of the aliphatic hydrocarbon effluent mixtures, cited in Table 3, was verified visually.

TABLE 4. DETECTOR RESPONSES TO SELECTED ORGANICS*

Organic	Rotameter Setting ≠ (mm)	Calculated Conc (ppm organic)	Detector Response Sigrist+ (ppm)	Detector Response Invalco (ppm)
KHP (6.1%) in H_2O	50	4.9	N	23
	100	11.2	N	45
	150	25.4	N	117
Resorcinol (25%) in H_2O	150	104	0.6	158
	100	45.9	0.2	78
	50	20.0	N	38
Methanol	150	--	N	N

* Organics of reagent-grade quality were used in this detector checkout test conducted with room-temperature water.

≠ A Brooks R-2-15-AA-SS rotameter was used for each of the fluids.

\+ An FLJ-5 reference cell was used in the Sigrist.

N = Negligible (less than 0.1 ppm).

A second item of interest is the Sigrist detection of resorcinol in water, the first indication of the Sigrist responding to a known concentration of fluorescent material. The fact that the Sigrist measurement indicates only a fraction of the calculated resorcinol input is not considered a serious drawback; of more importance is the ability of the device to repeatably obtain the same response for a fixed concentration of a given chemical.

DF-2/KHP

Since a requirement of the multidetector concept is the quantification of a known petroleum oil in the presence of interferent(s), it was considered important to demonstrate the viability of the technique at an early stage in the program. Proof of concept was provided by a series of flow runs involving Diesel Fuel 2 (DF-2), potassium biphthalate (KHP), and room-temperature tap water. Data from the flow runs appear in Table 5. The runs were conducted with the FLJ-10 reference cell in the Sigrist and two R-2-15-AA-SS rotameters for DF-2 and KHP. The DF-2 fuel blend is a commercial grade produced by Chevron (Standard Oil of California). The reagent-grade KHP was introduced as a 6.1% (by weight) aqueous solution.

The data show that over a DF-2 concentration range from 10 to 150 ppm repetitive runs of DF-2 in water, as measured by the Sigrist and Invalco devices, provide reproducible responses. This fact, coupled with the knowledge that DF-2 produces a relatively respectable response in the Sigrist, unlike the rather weak resorcinol response (see Table 4), and is readily available commercially, means that DF-2 is a prime candidate for use as a "reference oil" for calibration/checkout of the multidetector system. A reference mixture, consisting primarily of refined petroleum products, that could be used to effect a suitable response in each of the three detectors that will ultimately comprise the multidetector system had been actively sought.

Another observation from the data in Table 5 involves the Invalco responses to KHP, which are somewhat lower than those obtained previously (see Table 4). The explanation may be found in the fact that more than a month elapsed between the two sets of measurements and during this period a serious "zero shift" problem was occurring. For a discussion of this problem, see this section, Multidetector Evaluation, Results and Discussion.

The most important conclusion evident from Table 5 data is that, using DF-2 as the known oil and KHP as the interferent, the devices are able to quantify DF-2 in the presence of KHP. The measured responses for the last set of data show that the Sigrist did not respond to the KHP while sensing the DF-2. If a minicomputer were to survey the Sigrist and Invalco responses of any single run in the last data set for the lower value produced by the two devices (based on the previous DF-2 calibration data and the belief that the contribution of an interferent such as KHP would be additive), it would select the Sigrist response value. The minicomputer would then compute the actual concentration using the DF-2 calibration data.

It might also be noted that if the KHP contribution is subtracted (by using the KHP calibration data) from each Invalco measured response to the DF-2/KHP mixture in the last data set, the remaining DF-2 contribution

TABLE 5. DETECTOR RESPONSES TO DF-2/KHP*

DF-2		KHP		Measured Response	
Rotameter≠ Setting (mm)	Conc (ppm)	Rotameter≠ Setting (mm)	Conc (ppm)	Sigrist+ Total (ppm)	Invalco Total (ppm)
150	147	-	-	5.4	152
100	57	-	-	1.5	35
50	26	-	-	0.6	12
15	11	-	-	0.3	5
150	147	-	-	5.2	150
100	57	-	-	1.3	38
50	26	-	-	0.5	12
15	11	-	-	0.3	5
15	11	-	-	0.3	6
50	26	-	-	0.5	11
100	57	-	-	1.2	37
150	147	-	-	5.1	148
-	-	150	25	N	79
-	-	100	11	N	34
-	-	50	5	N	13
-	-	15	2	N	5
-	-	50	5	N	13
-	-	100	11	N	37
-	-	150	25	N	83
100	57	-	-	1.3	38
100	57	150	25	1.3	115
100	57	100	11	1.3	81
100	57	50	5	1.3	56
100	57	-	-	1.3	38

* A commercial grade of Diesel Fuel 2 (DF-2) produced by Chevron and a 6.1% (by weight) aqueous solution of reagent-grade potassium biphthate (KHP) were used in this detector response test conducted with room-temperature tap water.

≠ Separate Brooks R-2-15-AA-SS rotameters were used for the DF-2 and KHP fluids.

+ An FLJ-10 reference cell was used in the Sigrist.

N = Negligible (less than 0.1 ppm).

averages 40.7 ppm, in close agreement with the measured DF-2 response of 38 ppm.

MULTIDETECTOR EVALUATION

A comprehensive evaluation of the selected oil meters was critically conducted under laboratory conditions to identify their ability to accurately and specifically detect and quantify petroleum oil in fresh, brackish, or sea water over the temperature and concentration ranges listed by the manufacturer. The selected devices were tested with water contaminated with petroleum oil and possible interfering materials such as organics, vegetable oils, dissolved solids, and detergents to demonstrate the feasibility of the integrated package to quantify petroleum oil in water despite the presence of such interfering substances. The experimental effort also provided information on the sensitivity, linearity and accuracy, repeatability, response speed, and reliability of the selected oil monitors.

Response Data

Flow tests of the preprototype multidetector system were delayed until arrival of the Horiba OCMA-25 replacement for the originally ordered 0-200 ppm range OCMA-32A. Upon discovery that the delivered OCMA-25 had an oil content range of 0-20 ppm, the possibility of an "overrange" problem seemed inevitable.

Initial flow tests conducted with all three detectors on stream and using DF-2 as the known oil and isooctane as the interferent confirmed the Horiba "overrange" problem. In this respect, the "overrange" alarm shuts the sample pump down when oil content readings exceed 25 ppm, thus extending the useful life of the absorbent but, at the same time, restricting meaningful data to oil concentrations well below this level. To obtain meaningful data with the Horiba, lower-flowrate rotameters were calibrated and installed in the flow loop. A second interferent reservoir/rotameter subsystem was added to the flow loop so that benzene and/or isooctane could be introduced into the flow stream containing known oil. Subsequent flow tests verified the utility of the added reservoir whereas the change to smaller rotameter tube sizes produced only slight improvement in providing reliable oil/interferent levels at concentrations low enough for the Horiba.

After several unsuccessful attempts to obtain information from Horiba on conversion of the OCMA-25 to a 0-100 ppm range device, the decision was made (and agreed to by Horiba) to modify the internal sample-to-solvent ratio (originally 2:1) by reversing the pump module and reconnecting the various inflow and outflow lines accordingly. Additional details can be found in this section under Calibrations, Detectors. During the course of multidetector evaluation tests with DF-2 and Gulf crude oil as the known oils, the Horiba was evaluated with and without internal acid injection.

Diesel Fuel 2--

With the above-noted hardware changes in effect, useful data from all three devices were obtained with DF-2 at a number of concentration levels and in the presence of benzene and isooctane. The effects of temperature, dissolved solids (synthetic sea water), vegetable oil, and detergent were also

investigated. Tabulations of the data are presented here, while a discussion of the results is found in this section under Multidetector Evaluation, Results and Discussion.

All important flow system parameters appear in each table. Each table also lists the time, temperature, indicated response, calculated rotameter concentration, and corrected response concentration for each individual flow test, i.e., each different set of rotameter conditions. The run designation, a brief description and the table number for each set of DF-2 flow tests are as follows:

Run	Description	Table
A	Stagnant (24 hours) and fresh tap water at room temperature (r.t.) (w/o Horiba acid injection)	6
B	Fresh tap water at 30°C (w/o Horiba acid injection)	7
C	Fresh tap water at 10°C; fresh tap water at r.t. (w/o Horiba acid injection)	8
D	Synthetic sea water at 30°C; fresh tap water at r.t. (w/o Horiba acid injection)	9
E	Synthetic sea water at 15°C; fresh tap water at r.t. (w/o Horiba acid injection)	10
L	Fresh tap water at r.t. and olive oil (w/Horiba acid injection)	11
M	Fresh tap water and detergent-loaded water at r.t. (w/Horiba acid injection)	12

Synthetic sea water mixtures, used in Runs D and E, were prepared by adding 7.56 kg (16.7 lbs) of Utility Marine Mix supplied by the Utility Chemical Company (Paterson, New Jersey) to a few liters of hot water with stirring and then transferring the partially dissolved mixture into 0.19 m^3 (50 gal) of tap water in a water-reservoir drum. Since the contents of the drum required periodic mixing to effectively dissolve the solids, the usual approach was to let the solids dissolve overnight.

Detergent-loaded water used in Run M was prepared by adding 1.9 ml of Liqui-Nox, a biodegradable, phosphate-free laboratory detergent manufactured by Alconox, Inc. (New York, New York) to 0.19 m^3 (50 gal) of fresh tap water in one of the two water reservoir drums. The other drum was loaded with fresh tap water, which with the detergent-loaded water was alternately fed through the flow loop to the detectors.

The olive oil used as an interferent in Run L is produced and marketed as "Olio sasso" by P. Sasso e Tigli of Oneglia, Italy, and was introduced into the flow loop through one of the interferent reservoir subsystems.

TABLE 6. DETECTOR RESPONSES TO DF-2 - RUN A*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Isooctane ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
8:43:00	20.7	8.5	31.5	0.0	--	--	--	--	0.0	0.0	0.0
8:47:45	20.5	11.7	35.3	1.3	4.2	--	--	4.2	4.8	0.19	5.2
8:51:00	20.6	15.5	39.0	3.36	9.8	--	--	9.8	10.5	0.37	13.4
8:54:30	20.6	19.3	42.0	4.86	16.5	--	--	16.5	16.2	0.52	19.4
8:59:30	20.6	24.7	48.0	7.44	23.5	--	--	23.5	24.3	0.82	29.8
9:03:30	20.6	67.1	48.0	8.04	23.5	54.9	--	78.4	87.9	0.82	32.2
9:06:15	20.6	86.1	48.4	7.78	23.5	115.0	--	138.5	116.4	0.84	31.1
9:06:30	Start tap water replenishment										
9:07:15	20.6	88.0	48.0	8.00	23.5	117.2	--	140.7	119.3	0.82	32.0
9:12:15	18.3	25.5	44.5	7.32	23.5	--	--	23.5	24.0	0.79	29.3
9:15:45	Horiba manual reset										
9:19:30	17.6	35.0	41.0	12.08	23.5	--	19.5	43.0	38.3	0.75	48.3
9:27:00	17.5	40.0	38.4	16.06	23.5	--	33.6	57.1	45.8	0.62	64.2
9:37:30	17.5	79.0	38.0	16.92	23.5	54.9	34.5	113.0	104.3	0.60	67.7
9:47:15	17.5	94.0	38.5	17.26	23.5	113.5	33.3	170.4	126.8	0.62	69.0
9:56:45	17.6	36.5	38.5	13.68	23.5	--	26.6	50.1	40.5	0.62	54.7
10:06:45	17.6	41.0	37.5	16.14	23.5	--	33.3	56.8	47.3	0.57	64.6
10:21:45	17.6	22.5	41.5	7.40	23.5	--	--	23.5	19.5	0.77	29.6
10:28:00	17.6	27.5	46.5	9.50	31.6	--	--	31.6	27.0	1.02	38.0
10:35:30	17.6	9.5	26.0	0.0	--	--	--	--	0.0	0.0	0.0

* Run A was conducted with STAGNANT (24 HRS) TAP WATER AT ROOM TEMPERATURE, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15AA-sapphire, benzene, R-2-15AAA-SS, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 7. DETECTOR RESPONSES TO DF-2 - RUN B*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
13:37:00	29.9	13.5	26.4	0.0	--	--	--	0.0	0.0	0.0
13:44:45	29.8	17.3	30.1	1.20	4.2	--	4.2	5.7	0.18	4.8
13:49:45	29.7	20.5	33.5	2.92	9.8	--	9.8	10.5	0.35	11.7
13:55:00	29.6	26.0	37.1	4.56	16.5	--	16.5	18.8	0.53	18.2
13:58:00	29.6	31.0	42.0	6.88	23.5	--	23.5	26.3	0.78	27.5
14:00:30	29.5	37.0	47.0	9.28	31.6	--	31.6	35.3	1.03	37.1
14:03:00	29.3	94.5	50.0	9.38	31.6	106.9	138.5	121.5	1.18	37.5

* Run B was conducted with FRESH TAP WATER AT 30°C. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-sapphire, benzene, R-2-15-AAA-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 8. DETECTOR RESPONSES TO DF-2 - RUN C*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
15:18:00	9.9	11.5	28.0	0.0	--	--	--	0.0	0.0	0.0
15:29:00	10.0	16.5	37.0	3.46	10.9	--	10.9	7.5	0.45	13.8
15:32:45	10.1	18.0	40.0	4.48	16.1	--	16.1	9.8	0.60	17.9
15:38:45	10.2	23.5	47.0	7.12	23.5	--	23.5	18.0	0.95	28.5
15:42:45	10.3	27.3	52.0	9.54	31.6	--	31.6	23.7	1.20	38.2
15:49:00	11.1	91.0	55.0	11.24	33.0	106.2	139.2	119.3	1.35	45.0
15:49:15	Start tap water replenishment									
16:01:00	19.4	92.5	54.8	10.34	33.0	106.2	106.2	123.0	1.21	41.4
16:10:00	18.8	30.0	50.3	10.04	33.2	--	33.2	29.3	0.99	40.2
16:16:00	18.2	19.5	41.5	5.18	17.5	--	17.5	13.5	0.55	20.7
16:34:00	17.6	10.5	30.5	0.0	--	--	--	0.0	0.0	0.0

* Run C was conducted with FRESH TAP WATER AT 10°C, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-sapphire, benzene, R-2-15-AAA-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 9. DETECTOR RESPONSES TO DF-2 - RUN D*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Isooctane ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
14:18:30	29.1	23.2	33.7	0.0	--	--	--	--	0.0	0.0	0.0
14:26:30	29.4	30.0	40.0	2.26	10.2	--	--	10.2	10.2	0.31	9.0
14:30:30	29.4	37.0	45.0	4.42	16.5	--	--	16.5	20.7	0.55	17.7
14:35:15	29.4	42.4	49.0	6.60	24.6	--	--	24.6	28.8	0.76	26.4
14:39:00	29.3	49.0	55.0	8.72	33.2	--	--	33.2	38.7	1.06	34.9
14:41:15	29.2	97.5	55.5	9.46	31.6	105.5	--	137.1	111.5	1.09	37.8
14:44:15	Start tap water replenishment										
15:12:00	17.1	46.0	48.5	14.28	32.3	--	22.1	54.4	48.8	0.85	57.1
15:20:15	17.7	34.0	53.5	9.5	33.0	--	--	33.0	30.8	1.10	38.0
15:37:15	17.7	13.5	31.5	0.0	--	--	--	--	0.0	0.0	0.0

* Run D was conducted with SYNTHETIC SEAWATER AT 30°C, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-sapphire, benzene, R-2-15-AAA-SS, isooctane R-2-15-AAA-glass; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 10. DETECTOR RESPONSES TO DF-2 - RUN E*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Isooctane ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
9:05:00	16.1	19.4	36.6	0.0	--	--	--	--	0.0	0.0	0.0
9:08:00	15.3	25.0	43.0	2.56	10.5	--	--	10.5	8.4	0.32	10.2
9:12:00	15.0	27.0	45.5	3.36	15.4	--	--	15.4	11.4	0.44	13.4
9:15:45	15.1	33.0	52.0	5.86	23.5	--	--	23.5	20.4	0.77	23.4
9:22:45	14.9	37.0	57.0	8.10	31.6	--	--	31.6	26.4	1.07	32.4
9:27:15	14.5	96.5	60.0	9.96	33.0	107.0	--	140.0	115.7	1.17	39.8
9:29:45	14.0	102.0	52.5	17.48	33.2	107.0	33.3	173.5	123.9	0.79	69.9
9:30:00	Start tap water replenishment										
9:42:00	17.3	103.0	47.0	19.44	32.3	107.0	35.4	174.6	135.0	0.85	77.8
9:48:45	17.4	93.0	53.5	10.16	31.6	107.0	--	138.5	120.0	1.17	40.6
9:54:45	17.4	31.5	51.0	8.96	32.3	--	--	32.3	27.8	1.05	35.8
10:06:30	17.4	13.0	30.0	0.0	--	--	--	--	0.0	0.0	0.0

* Run E was conducted with SYNTHETIC SEAWATER AT 15°C, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-sapphire, benzene, R-2-15-AAA-SS, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 11. DETECTOR RESPONSES TO DF-2 - RUN L*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: DF-2 ppm	Rotameter Concentration: Olive Oil ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
17:02:45	18.1	20.0	28.0	0.0	--	--	--	0.0	0.0	0.0
17:20:00	18.0	29.0	43.0	4.6	26.0	--	26.0	13.5	0.75	18.4
17:25:15	17.9	52.0	71.5	14.76	71.6	--	71.6	48.0	2.17	59.0
17:42:15	17.9	54.5	65.5	16.58	71.6	8.5	80.1	53.3	1.87	66.3
17:54:30	17.9	49.5	62.0	14.00	71.6	--	71.6	47.3	1.70	56.0
18:06:30	17.9	16.7	28.0	0.0	--	--	--	0.0	0.0	0.0

* Run L was conducted with FRESH TAP WATER (AND OLIVE OIL) AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-SS, olive oil, R-2-15-D-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ With acid injection.

TABLE 12. DETECTOR RESPONSES TO DF-2 - RUN M*

Time	Temperature °C	Input Medium	Indicated Response Invalco % FS	Indicated Response Sigrist % FS	Indicated Response Horiba ppm_v ≠	Rotameter Concentration DF-2 ppm	Rotameter Concentration Detergent ppm	Rotameter Concentration Total ppm	Corrected Response Invalco ppm	Corrected Response Sigrist ppm	Corrected Response Horiba ppm_v
11:27:00	18.0	Fresh water	18.0	29.0	0.0	--	--	--	0.0	0.0	0.0
11:31:45	19.0	Detergent	20.5	29.0	0.0	--	10.0	10.0	3.8	0.0	0.0
11:35:30	18.0	Fresh	18.3	29.0	0.0	--	--	--	0.5	0.0	0.0
11:44:30	18.0	Fresh	42.3	66.5	10.34	52.6	--	52.6	36.5	1.88	41.4
11:49:30	19.1	Detergent	47.0	60.0	10.54	50.9	10.0	60.9	43.5	1.55	42.2
11:54:30	19.4	Detergent	22.1	31.7	1.20	--	10.0	10.0	4.7	0.14	4.8
12:06:00	17.9	Fresh	18.0	29.3	0.0	--	--	--	0.0	0.0	0.0

* Run M was conducted with FRESH AND DETERGENT-LOADED TAP WATER AT ROOM TEMPERATURE. The detergent used was Liqui-Nox, manufactured by Alconox Inc. (New York, NY). Flow system parameters were: Sigrist ref. cell, FLJ-5; rotameters, DF-2, R-2-15-AA-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ With acid injection.

Except for stagnant and fresh tap water runs at room temperature, the water preparations were usually circulated through the flow loop back to the water reservoir drum(s) before use in the flow runs. This procedure was designed to produce more uniform, representative water mixtures.

Gulf Crude Oil--

Useful data from all three devices were obtained with Gulf crude oil (from Shell Platform SM130B in the Morgan City, Louisiana, grid) at a number of concentration levels and in the presence of benzene and isooctane. The effects of temperature, dissolved solids (synthetic sea water) and vegetable oil were also investigated. The data are presented here, while a discussion of the results is found in this section under Multidetector Evaluation, Results and Discussion.

All important flow parameters appear in each table. Each table also lists the time, temperature, indicated response, calculated rotameter concentration, and corrected response concentration for each individual flow run, i.e., each different set of rotameter conditions. The run designation, a brief description, and the table number for each set of Gulf crude oil flow tests are as follows:

Run	Description	Table
F	Stagnant (24 hours) and fresh tap water at r.t. (w/o Horiba acid injection)	13
G	Fresh tap water at 30°C; fresh tap water at r.t. (w/o Horiba acid injection)	14
H	Synthetic sea water at r.t.; fresh tap water at r.t. (w/o Horiba acid injection)	15
I	Fresh tap water at r.t. (w/ and w/o Horiba acid injection)	16

Run	Description	Table
J	Fresh tap water at r.t. (w/Horiba acid injection)	17
K	Stagnant (48 hours) tap water at r.t. and olive oil (w/Horiba acid injection)	18

TABLE 13. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN F*

Time	Temperature °C	Indicated Response			Rotameter Concentration				Corrected Response		
		Invalco % FS	Sigrist % FS	Horiba ppm_v ≠	Crude Oil ppm	Benzene ppm	Isooctane ppm	Total ppm	Invalco ppm	Sigrist ppm	Horiba ppm_v
10:08:00	19.6	14.0	0.5	-0.20	--	--	--	--	0.0	0.0	0.0
10:19:00	19.6	20.1	13.0	1.74	7.5	--	--	7.5	9.2	12.5	7.8
10:24:30	19.7	30.0	31.0	4.40	22.6	--	--	22.6	24.0	30.5	18.4
10:26:30	19.7	Start tap water replenishment									
10:29:45	18.3	52.0	67.0	12.10	60.3	--	--	60.3	57.0	66.5	49.2
10:44:30	17.4	27.5	26.0	4.64	22.3	--	--	22.3	20.3	25.5	19.4
10:49:30	17.4	90.0	35.0	5.10	18.7	102.6	--	121.2	114.0	34.5	21.2
10:57:30	17.3	102.0	33.0	13.04	17.2	102.6	32.2	151.9	132.0	32.5	53.0
11:03:30	17.3	89.0	31.0	4.96	17.2	102.6	--	119.8	112.5	30.5	20.6
11:11:45	17.3	26.0	22.0	3.84	17.2	--	--	17.2	18.0	21.5	16.2
11:21:45	17.3	14.0	0.5	-0.20	--	--	--	--	0.0	0.0	0.0

* Run F was conducted with STAGNANT (24 HRS) TAP WATER AT ROOM TEMPERATURE, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, benzene, R-2-15-AAA-SS, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 14. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN G*

Time	Temperature °C	Indicated Response			Rotameter Concentration			Corrected Response		
		Invalco % FS	Sigrist % FS	Horiba ppm_v ≠	Crude Oil ppm	Benzene ppm	Total ppm	Invalco ppm	Sigrist ppm	Horiba ppm_v
15:38:00	29.8	20.0	0.5	-0.20	--	--	--	0.0	0.0	0.0
15:51:45	29.6	27.0	13.0	2.48	8.3	--	8.3	10.5	12.5	10.7
15:56:30	29.6	37.0	30.0	5.28	22.6	--	22.6	25.5	29.5	21.9
16:03:15	29.4	57.0	65.0	11.88	51.7	--	51.7	55.5	64.5	48.3
16:05:30	Start tap water replenishment									
16:09:30	19.1	118.0	85.0	11.66	48.5	106.2	154.7	147.0	84.5	47.4
16:13:30	18.3	55.0	64.5	11.92	49.6	--	49.6	52.5	64.0	48.5
16:23:45	18.1	19.0	0.5	-0.20	--	--	--	0.0	0.0	0.0

* Run G was conducted with FRESH TAP WATER AT 30°C, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, benzene, R-2-15-AAA-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 15. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN H*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v ≠	Rotameter Concentration: Crude Oil ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Isooctane ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v
9:42:00	22.9	22.8	0.7	-0.20	--	--	--	--	0.0	0.0	0.0
9:46:45	22.7	29.5	13.5	1.98	8.3	--	--	8.3	10.1	12.8	8.7
9:52:30	22.7	41.0	30.0	4.38	22.3	--	--	22.3	27.3	29.3	18.3
9:58:00	22.5	65.0	67.0	10.40	54.6	--	--	54.6	63.3	66.3	42.4
10:02:00	22.2	104.4	78.5	10.88	53.2	65.9	--	119.1	122.4	77.8	44.3
10:07:15	21.9	122.6	86.0	10.42	51.7	117.2	--	168.9	149.7	85.3	42.5
10:07:45	Start tap water replenishment										
10:14:15	18.0	77.5	82.0	18.24	54.2	--	25.4	79.6	93.0	81.5	73.8
10:22:15	17.5	50.5	56.5	11.94	54.2	--	--	54.2	52.5	56.0	48.6
10:32:45	17.4	15.5	0.5	-0.20	--	--	--	--	0.0	0.0	0.0

* Run H was conducted with SYNTHETIC SEAWATER AT ROOM TEMPERATURE, followed by FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, benzene, R-2-15-AAA-SS, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24 x 10^5 Pa (32.5 psig); inlet pressure, Invalco 1.5 x 10^5 Pa (7.0 psig), Sigrist, 1.5 x 10^5 Pa (7.0 psig), Horiba, 1.1 x 10^5 Pa (1.5 psig).

≠ No acid injection.

TABLE 16. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN I*

Time	Temperature °C	Indicated Response: Invalco % FS	Indicated Response: Sigrist % FS	Indicated Response: Horiba ppm_v	Rotameter Concentration: Crude Oil ppm	Rotameter Concentration: Benzene ppm	Rotameter Concentration: Isooctane ppm	Rotameter Concentration: Total ppm	Corrected Response: Invalco ppm	Corrected Response: Sigrist ppm	Corrected Response: Horiba ppm_v	Horiba Acid Injection
10:44:00	18.3	17.0	0.5	-0.30	--	--	--	--	0.0	0.0	0.0	No
11:00:00	18.1	23.0	15.0	2.20	9.0	--	--	9.0	9.0	14.5	10.0	Yes
11:04:00	18.1	23.0	15.0	2.02	9.0	--	--	9.0	9.0	14.5	9.3	No
11:14:00	18.1	30.5	29.0	5.24	22.3	--	--	22.3	20.3	28.5	22.2	No
11:16:45	17.7	30.0	29.0	5.24	22.3	--	--	22.3	19.5	28.5	22.2	Yes
11:24:15	17.7	47.0	55.0	10.30	48.5	--	--	48.5	45.0	54.5	42.4	Yes
11:30:15	17.7	47.0	55.0	9.92	48.5	--	--	48.5	45.0	54.5	40.9	No
13:34:30	17.7	104.6	68.0	11.26	47.1	86.4	--	133.5	131.4	67.5	46.2	No
11:40:30	17.7	104.7	68.0	11.18	47.1	85.0	--	132.0	131.6	67.5	45.9	Yes
11:53:00	17.7	118.8	78.0	18.48	46.7	85.0	28.3	160.0	152.7	77.5	75.1	Yes
11:56:00	17.7	117.2	78.0	18.26	46.7	85.0	28.0	159.7	150.3	77.5	74.2	No
12:03:15	17.7	68.0	66.0	12.12	47.1	--	21.0	68.0	76.5	65.5	49.7	Yes
12:10:45	17.7	48.0	55.0	10.76	47.8	--	--	47.8	46.5	54.5	44.2	Yes
12:22:30	18.0	16.5	1.0	-0.30	--	--	--	--	0.0	0.0	0.0	No

* Run I was conducted with FRESH TAP WATER AT ROOM TEMPERATURE (with and without HORIBA ACID INJECTION). Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, benzene, R-2-15-AAA-SS, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24 x 10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5 x 10^5 Pa (7.0 psig), Sigrist, 1.5 x 10^5 Pa (7.0 psig), Horiba, 1.1 x 10^5 Pa (1.5 psig).

TABLE 17. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN J*

Time	Temperature °C	Indicated Response Invalco % FS	Sigrist % FS	Horiba ppm_v ≠	Rotameter Concentration Crude Oil ppm	Isooctane ppm	Total ppm	Corrected Response Invalco ppm	Sigrist ppm	Horiba ppm_v
15:27:45	18.6	16.5	0.5	-0.28	--	--	--	0.0	0.0	0.0
15:38:15	18.5	23.3	0.5	6.10	--	31.0	31.0	10.2	0.0	25.5
15:39:00	18.4	23.0	0.5	6.10	--	31.0	31.0	10.1	0.0	25.1
15:45:45	18.4	16.3	0.5	-0.18	--	--	--	0.0	0.0	0.0
15:46:15	18.3	16.2	0.5	-0.28	--	--	--	0.0	0.0	0.0
15:53:45	18.2	28.0	23.0	4.04	17.2	--	17.2	17.7	22.5	17.3
15:54:45	18.2	28.0	23.0	4.14	17.2	--	17.2	17.7	22.5	17.7
16:05:45	18.1	51.5	60.0	11.92	52.4	--	52.4	53.1	59.5	48.2
16:06:30	18.2	51.5	60.0	12.08	52.4	--	52.4	53.1	59.5	48.8
16:18:00	18.1	16.0	0.5	-0.12	--	--	--	0.0	0.0	0.0

* Run J was conducted with FRESH TAP WATER AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, isooctane, R-2-15-AAA-glass; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ With acid injection.

TABLE 18. DETECTOR RESPONSES TO GULF CRUDE OIL - RUN K*

Time	Temperature °C	Indicated Response Invalco % FS	Sigrist % FS	Horiba ppm_v	Rotameter Concentration Crude Oil ppm	Olive Oil ppm	Total ppm	Corrected Response Invalco ppm	Sigrist ppm	Horiba ppm_v
14:33:00	18.0	17.5	0.5	0.14	--	--	--	0.0	0.0	0.0
14:47:30	17.8	20.5	0.5	1.84	--	7.1	7.1	4.5	0.0	6.8
14:58:45	17.8	33.0	27.5	5.86	15.1	7.1	22.2	23.6	27.0	22.9
15:16:45	17.9	35.0	27.0	6.48	15.1	9.2	24.3	26.7	26.5	25.4
15:25:00	17.9	28.5	20.0	3.88	15.1	--	15.1	17.3	19.5	15.0
15:46:45	17.7	17.0	0.5	0.14	--	--	--	0.0	0.0	0.0

* Run K was conducted with STAGNANT (48 HRS) TAP WATER (AND OLIVE OIL) AT ROOM TEMPERATURE. Flow system parameters were: Sigrist ref. cell, FLJ-100; rotameters, Gulf crude oil, R-2-15-D-sapphire, olive oil, R-2-15-D-SS; flow loop pressure, 3.24×10^5 Pa (32.5 psig); inlet pressure, Invalco, 1.5×10^5 Pa (7.0 psig), Sigrist, 1.5×10^5 Pa (7.0 psig), Horiba, 1.1×10^5 Pa (1.5 psig).

≠ With acid injection.

Comments regarding synthetic sea water formulations, olive oil, and the circulation of water preparations as described in regard to flow runs conducted with DF-2 also apply to the Gulf crude oil runs.

It should be noted that the DF-2 and Gulf crude oil data tabulated in Tables 6 through 18 are believed to be reliable data of good quality. Every attempt has been made to confirm the data that appears to be dubious. When anomalous data have been found, the original raw data traces and digitized data strips were scrutinized in a check of the data reduction process. Oftentimes, this produced a change in the original reduced value. Sometimes,

however, it reaffirmed the validity of the reported value.

Results and Discussion

It is evident from the data listed in this section under Multidetector Evaluation, Response Data, that the three selected oil-in-water detectors fail to measure up to their reputed ability to quantify petroleum oil in water on an individual basis. Although the devices detect DF-2 and Gulf crude oil, in some cases on a one-for-one basis, each fails to discriminate, to some extent, when interferents are present. There are specific instances, of course, where a particular device recognizes DF-2 or crude oil while ignoring a specific interferent that is present, but, in general, none of the devices is capable by itself of quantifying petroleum oil in water. The multidetector system is an obvious improvement but will require additional research to become truly effective. Suggestions for further improvements are discussed in Section 6. In the following paragraphs each of the three devices is thoroughly analyzed with respect to its response to interferents, sensitivity, linearity and accuracy, repeatability, response speed, and reliability. To accomplish this task, the data listed in Tables 6 through 18 have been utilized as they apply to each of the three detectors.

Sigrist--

With respect to overall capabilities, the Sigrist device appears more capable of quantifying petroleum oil in water with interferents present than the other two detectors. However, its capabilities are still too limited to do an effective job by itself. The reasons for these conclusions are found in the following paragraphs.

Interferents--Since the Sigrist responds only to compounds that fluoresce, in the case of petroleum oil, namely aromatics, many typical contaminants such as aliphatic and olefinic hydrocarbons do not produce, by themselves, a response in the Sigrist. This is demonstrated by the response data in Table 17, which shows no Sigrist response to isooctane and by the lack of Sigrist response in Table 18 to olive oil (by itself), rich in olefinic acids. However, in the presence of crude oil, isooctane and olive oil appear to enhance the Sigrist response, as can be seen by the response data in Tables 15 and 16 and Table 18, respectively. The reason for this synergistic effect is not known.

In addition, judging from the data in Table 12, detergent alone has no effect on the Sigrist, whereas the presence of detergent does appear to have a marginal suppressant effect on the Sigrist response to DF-2. It is also noted that residual DF-2 seems to remain detectable for a longer period of time after supply cutoff when a detergent is present. Not surprisingly, all the detectors appeared to exhibit this slow return to background in the presence of the detergent.

More serious, perhaps, (for the multidetector system) is the observation that an aliphatic hydrocarbon, such as isooctane, seems to quench or suppress the fluorescence from DF-2, as witnessed by the Sigrist responses in Tables 6, 9, and 10. This is probably because of the insolubility of isooctane in water, which results in a dispersion of small droplets of isooctane, effectively causing a partial blockage of incident and emitted UV radiation (to and from

the DF-2). The Sigrist also ignores the lower-boiling or single-ring aromatic compounds in the presence of DF-2, as can be seen by its negligible response to benzene exhibited in the DF-2 data, Tables 6 through 10. However, in the presence of Gulf crude oil (Tables 13 through 17), the Sigrist responds to benzene, again indicating a synergistic effect between the crude oil and the benzene that results in the response increase.

Sensitivity (Water and Temperature)--The Sigrist sensitivity can be examined by plotting its responses to DF-2 and Gulf crude oil. A plot of corrected response versus rotameter concentration for the Sigrist/DF-2 data from Tables 6 through 10 has resulted in the six linear curves seen in Figure 17. The most notable observation is, of course, the very low sensitivity of the Sigrist to DF-2. The Sigrist measures, on the average, a little over 3% of the DF-2. A relatively low response is not unexpected in that DF-2 aromatic content is usually limited, by specification, to a value not to exceed 20% to 25%.

Figure 17 also shows the effect of water type and temperature on the Sigrist response to DF-2. Except for curve (3), the remaining five curves are almost superimposed on each other. The Sigrist sensitivity to DF-2 appears, however, to decrease as sample fluid temperature increases, as indicated especially by the position of curve (3). In fact, curves (2) and (3) show the Sigrist is 20% more sensitive to DF-2 in fresh tap water at 10°C than at 30°C. This effect appears to be more pronounced in tap water than in synthetic sea water. However, at room temperature and above, dissolved solids (synthetic sea water) have no observable effect on Sigrist response to DF-2 as indicated by curves (2), (4), (5), and (6).

The effect of water type and temperature on the Sigrist response to Gulf crude oil has also been studied. A plot of the data from Tables 13 through 17 has produced four linear curves seen in Figure 18. Unlike the Sigrist/DF-2 data, the Sigrist/Gulf crude data shows that the sensitivity of the Sigrist to the crude is much greater, with an average response to rotameter concentration ratio of 1.2:1. Also, there appears to be a greater variation in response due to water type, especially as noted by the difference between Sigrist responses to Gulf crude in stagnant tap water (1) and fresh tap water (4). This translates to a 17% greater sensitivity to Gulf crude oil in stagnant tap water. There also appears to be a measurable, albeit small, effect due to dissolved solids in the tap water (synthetic sea water). This is evidenced by an 8% greater Sigrist response to Gulf crude oil in synthetic sea water (3) than in fresh tap water (4) at room temperature.

Linearity and Accuracy--The plots of Sigrist responses to DF-2 and Gulf crude oil versus rotameter concentrations, in Figures 17 and 18, respectively, were accomplished by computer in accordance with a least-squares linear curve fit. This choice of curve-fitting was selected due to the nature of the data and knowledge of the manufacturer's specifications for the detector outputs. The linear curves produced appear to be appropriate for the data. The corresponding correlation coefficients (coefficients of determination) resulting from the computer curve-fitting and the average error, $\pm \Sigma(\Delta y)/n$, of the data used in the development of each curve are listed in Table 19. The average error of the data is a measure of the precision of the system generating the

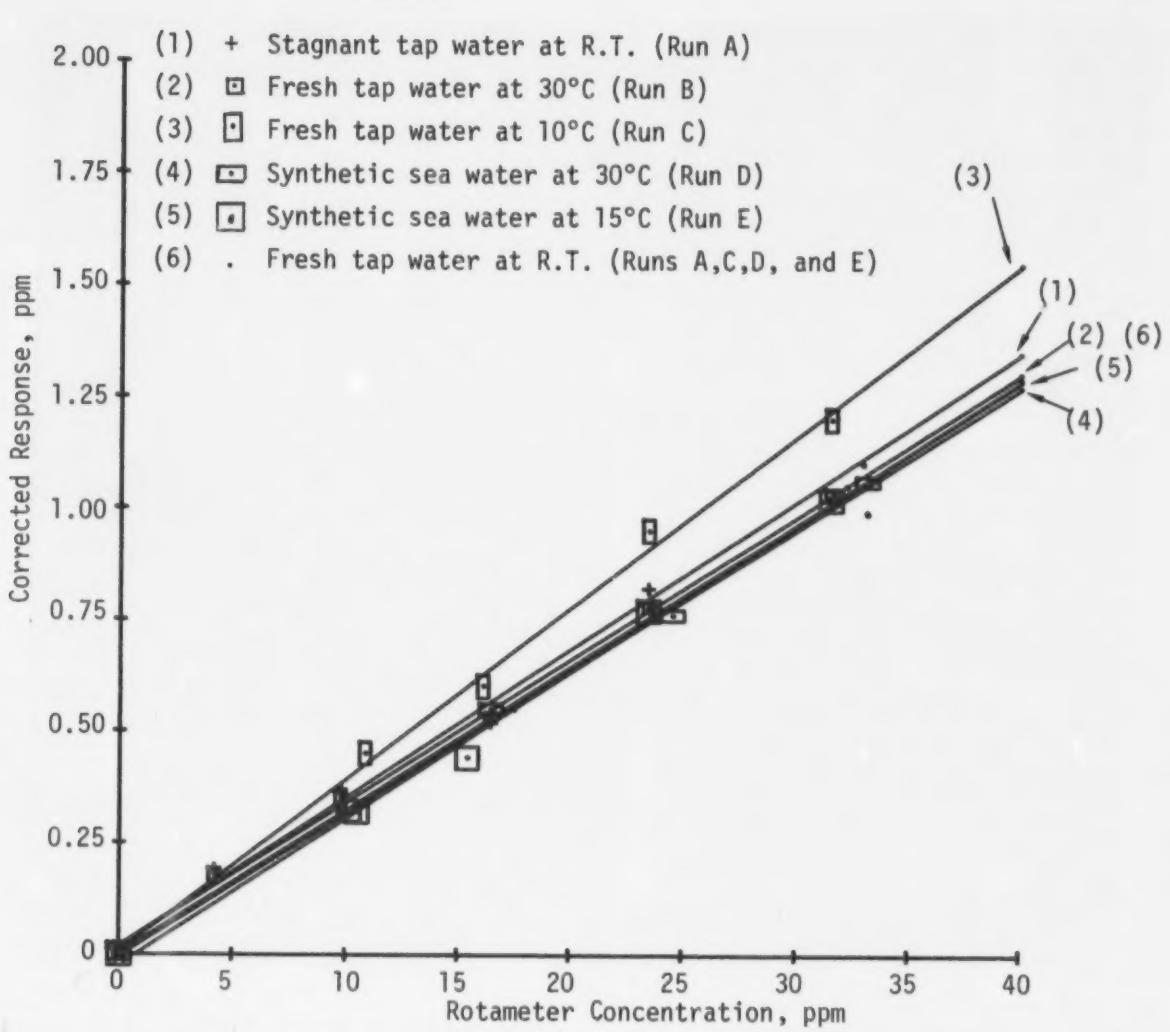

Figure 17. Effect of water type and temperature on Sigrist response to DF-2.

data. If systematic errors are eliminated (or compensated for by calibration) the average error of the data becomes a measure of the accuracy of the system. A minimum correlation coefficient of 0.995 is considered an indication of a good curve fit. The average error of the curve-fitted DF-2 data produced with the Sigrist is ±3.66%, while that of the curve-fitted Gulf crude oil data is ±3.97%. These values are higher than the manufacturer-claimed accuracy of ±2% FS; however, it should be noted that the operational characteristics of both the flow loop and the detector contribute to the average error.

Repeatability--The repeatability of a device can be defined as its ability

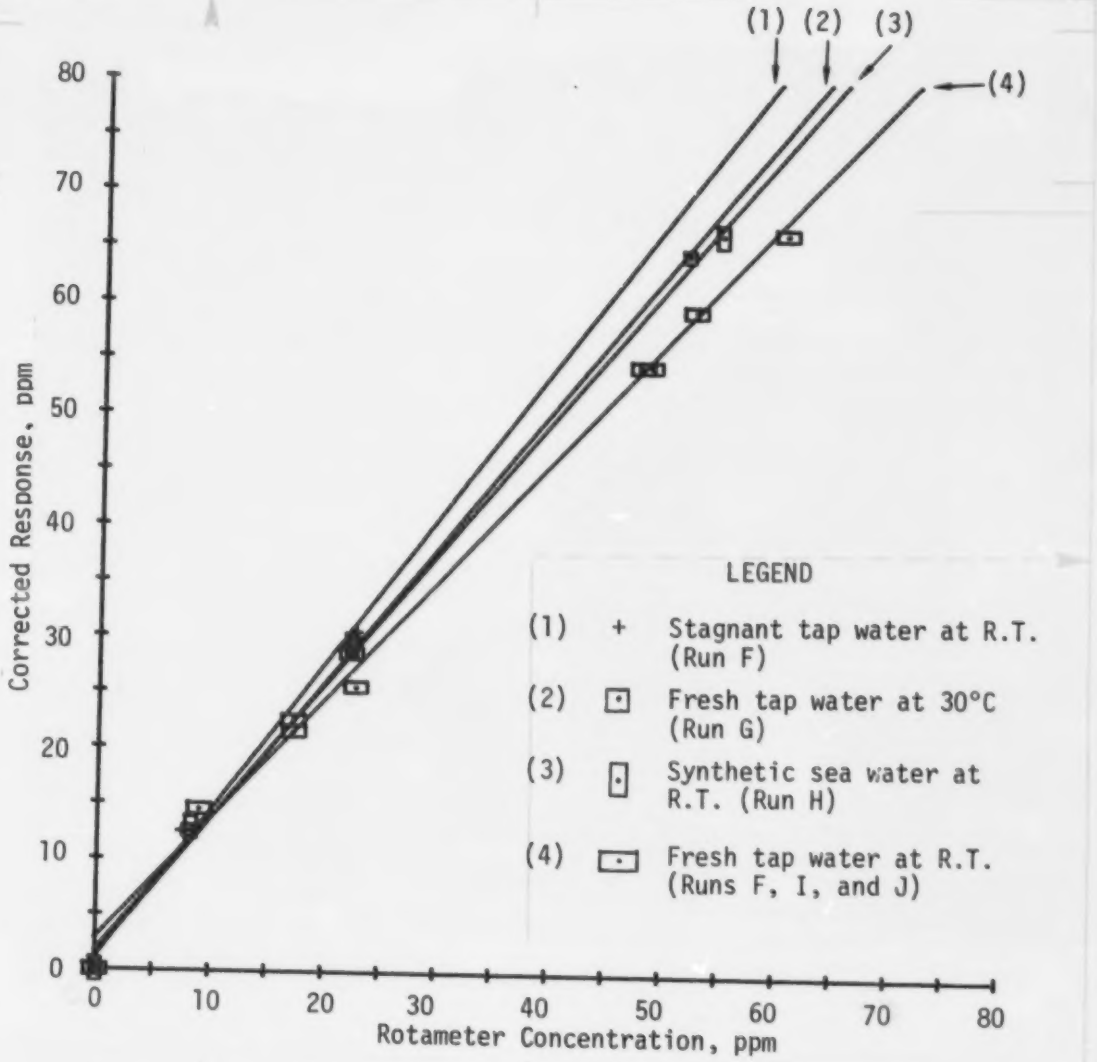

Figure 18. Effect of water type and temperature on Sigrist response to Gulf crude oil.

to produce the same response under the same conditions. A measure of this capability of the Sigrist can be found in an examination of its responses to Gulf crude oil in fresh tap water at room temperature, over a period of several days. The data are listed in Tables 13, 16, and 17. Since these data were obtained over several days under essentially the same experimental conditions, they provide a good measure of the Sigrist repeatability. A plot of the three sets of data is shown in Figure 19. The agreement among the three linear curves is excellent.

Response Speed--The Sigrist invariably detected the presence of a measurable additive in the flow stream within 15 to 30 seconds, while measuring 90%

TABLE 19. PRECISION OF SIGRIST LINEAR-CURVE-FITTED DATA

Curve (No.)	DF-2 Correlation Coefficient	DF-2 Error (± %)	Gulf Crude Oil Correlation Coefficient	Gulf Crude Oil Error (± %)
(1)	0.9886	7.00	0.9925	5.09
(2)	0.9978	3.92	0.9987	3.01
(3)	0.9961	3.16	0.9977	3.85
(4)	0.9981	2.41	0.9952	3.93
(5)	0.9953	2.81	--	--
(6)	0.9902	2.67	--	--

of the response change, in general, within 60 seconds. Upon additive shutoff, the Sigrist essentially reached background level in 30 seconds. These reaction times are, of course, as much a characteristic of the flow loop as of the detector.

Reliability--The only major malfunction of the device occurred shortly after it had been placed on stream. During a 100% reference check, the Sigrist stopped functioning. The response meter would not react to any input. Examination of the electrical system discovered the failure in the 20-volt power supply for the amplifier. The problem was traced to the emitter pin in the power supply circuit board. The pin was loose in the circuit board eyelet, apparently due to a cold solder joint. The joint was resoldered along with several other suspect joints. The problem never recurred.

Another problem that manifested itself a couple of times was a tendency for the null detection system to stick, probably caused by some dust or lint; however, it was felt that this was a minor problem.

It should be noted that the Sigrist is a very rugged device and easy to operate, factors that should enhance its appeal to operators in the field.

Invalco--

The Invalco does a good job quantifying petroleum oil-in-water without interferents present. In fact, the Invalco responds to most of the chemicals tested on a one-for-one basis, unlike the other two detectors. It is unfortunate that this characteristic is a major drawback to a multidetector petroleum oil-in-water monitoring system, i.e., it does not disciminate sufficiently. The reasons for these conclusions are found in the following paragraphs.

Interferents--Since the Invalco is based on the principle of UV absorption, it should be sensitive to aromatic compounds and various blends and

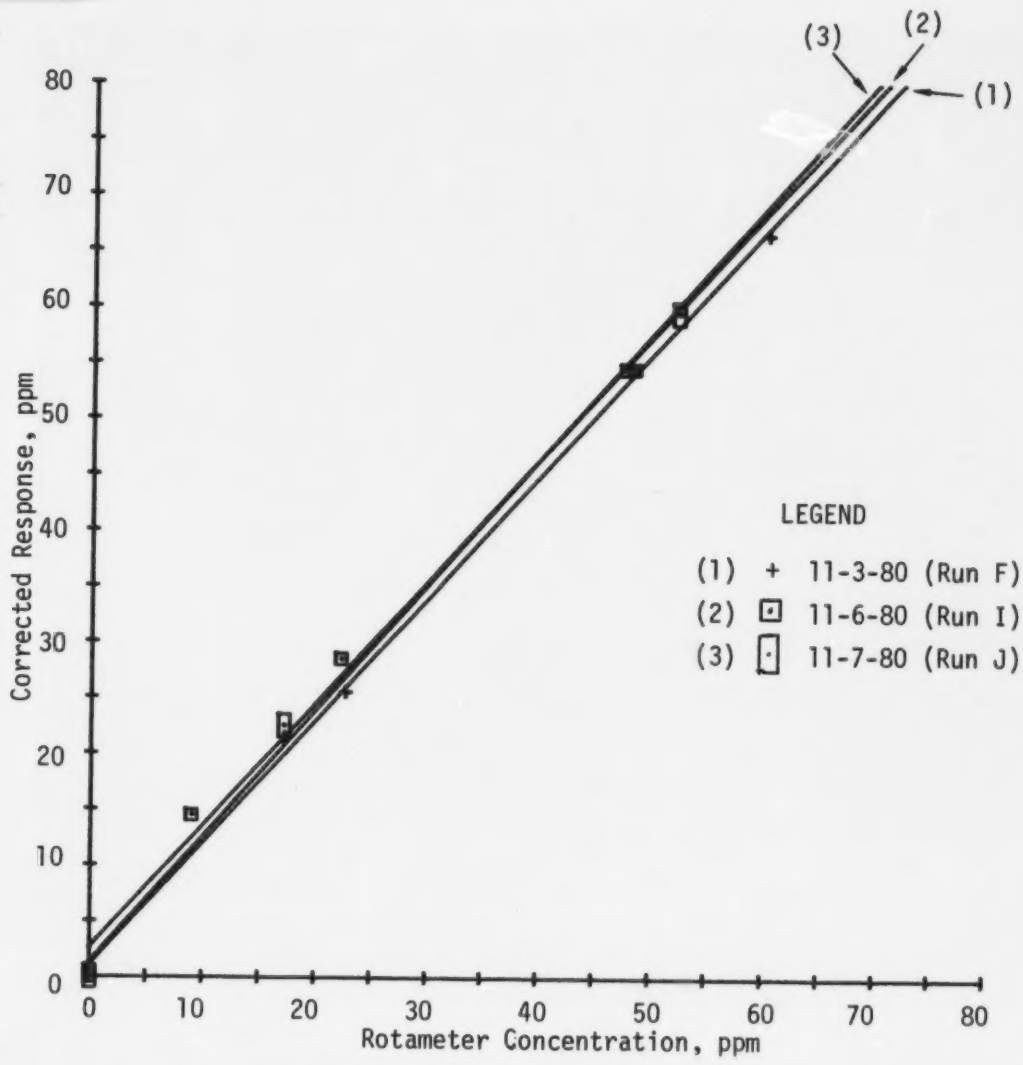

Figure 19. Effect of time on Sigrist response to Gulf crude oil in fresh tap water at room temperature.

mixtures to the extent that these compounds are present in them. This is the case as is testified to by the DF-2 data in Tables 6 through 10 and Gulf crude oil data in Tables 13 through 17. However, it should distinguish between aromatic and aliphatic hydrocarbons, but this is not the case, as can be seen by its response to isooctane (1) in the presence of DF-2, in Tables 6, 9, and 10, (2) in the presence of crude oil, in Tables 13, 15, and 16, and (3) by itself, in Table 17. Also, the Invalco should ignore olefinic hydrocarbons, such as olive oil, but it does not, as can be seen by the response data in Tables 11 and 18. This effect in the Invalco was observed before (see this section, Detector Checkout) when sizable responses were registered with aqueous dispersions of several aliphatic hydrocarbons. The evidence suggests that the device

is extremely sensitive to turbidity. In addition, it responds to detergent as indicated by the data in Table 12. At a DF-2 concentration of 50 ppm, the Invalco response is increased by 20% due to the presence of 10 ppm detergent, and, apparently, only half the increase is due to the detergent alone.

Sensitivity (Water and Temperature)--The Invalco sensitivity can be examined through plots of its responses to DF-2 and Gulf crude oil. A plot of corrected response versus rotameter concentration for the Invalco/DF-2 data from Tables 6 through 10 has produced six linear curves and they are depicted in Figure 20. These curves also show the effect of water type and temperature on the Invalco response to DF-2. They show that the Invalco sensitivity to DF-2, on the average, is very close to one-for-one. In fact, curve (1) has a slope of exactly one. Also, the curves exhibit a strong temperature dependency, with the Invalco less sensitive to DF-2 as the sample temperature decreases. This can be seen by comparing curves (2), (6), and (3), and curves (4) and (5). In fact, the Invalco is approximately 50% more sensitive to DF-2 in fresh tap water at 30°C than at 10°C. In addition, dissolved solids in tap water (synthetic sea water) enhance the Invalco sensitivity to DF-2 in fresh tap water at 30°C by about 5%.

A corrected response versus rotameter concentration plot of the Invalco/Gulf crude oil data from Tables 13 through 17 has resulted in four linear curves seen in Figure 21. Besides demonstrating the effect of water type and temperature on the Invalco response to Gulf crude oil, the curves also show that the Invalco sensitivity to Gulf crude is, on the average, a little greater than 1:1. In fact, curve (1) exhibits a slope of 1.05, rather similar to its sensitivity to DF-2, described above. Again, the curves show a temperature dependency in the same direction as with the DF-2, i.e., less sensitivity as fluid temperature decreases, though not as great. The response to Gulf crude is approximately 15% greater in fresh tap water at 30°C (2) than at room temperature (4). Also, dissolved solids in tap water (synthetic sea water) increases the Invalco sensitivity to Gulf crude in fresh tap water by about 25% at room temperature.

Linearity and Accuracy--The plots of Invalco responses to DF-2 and Gulf crude oil versus rotameter concentration, in Figures 20 and 21, respectively, were accomplished by computer in accordance with a least-squares linear curve fit. This choice of curve-fitting, as with the Sigrist data, was selected because of the manufacturer's specifications for a linear detector output. The resultant linear curves appear to appropriately describe the data.

The corresponding correlation coefficients (coefficients of determination) resulting from the computer curve-fitting and the average error of the data used in the development of each curve are listed in Table 20. The average error of this data is a measure of the precision of the system generating the data. If systematic errors are eliminated (or compensated for by calibration) the average error of the data becomes a measure of the accuracy of the system. A minimum correlation coefficient of 0.995 is considered an indication of a good curve fit. The average error of the curve-fitted DF-2 data produced with the Invalco is ±4.10%, while that of the curve-fitted Gulf crude oil data is ±2.78%. These values are actually better than the manufacturer-claimed accuracy of ±5% of oil content over the full range.

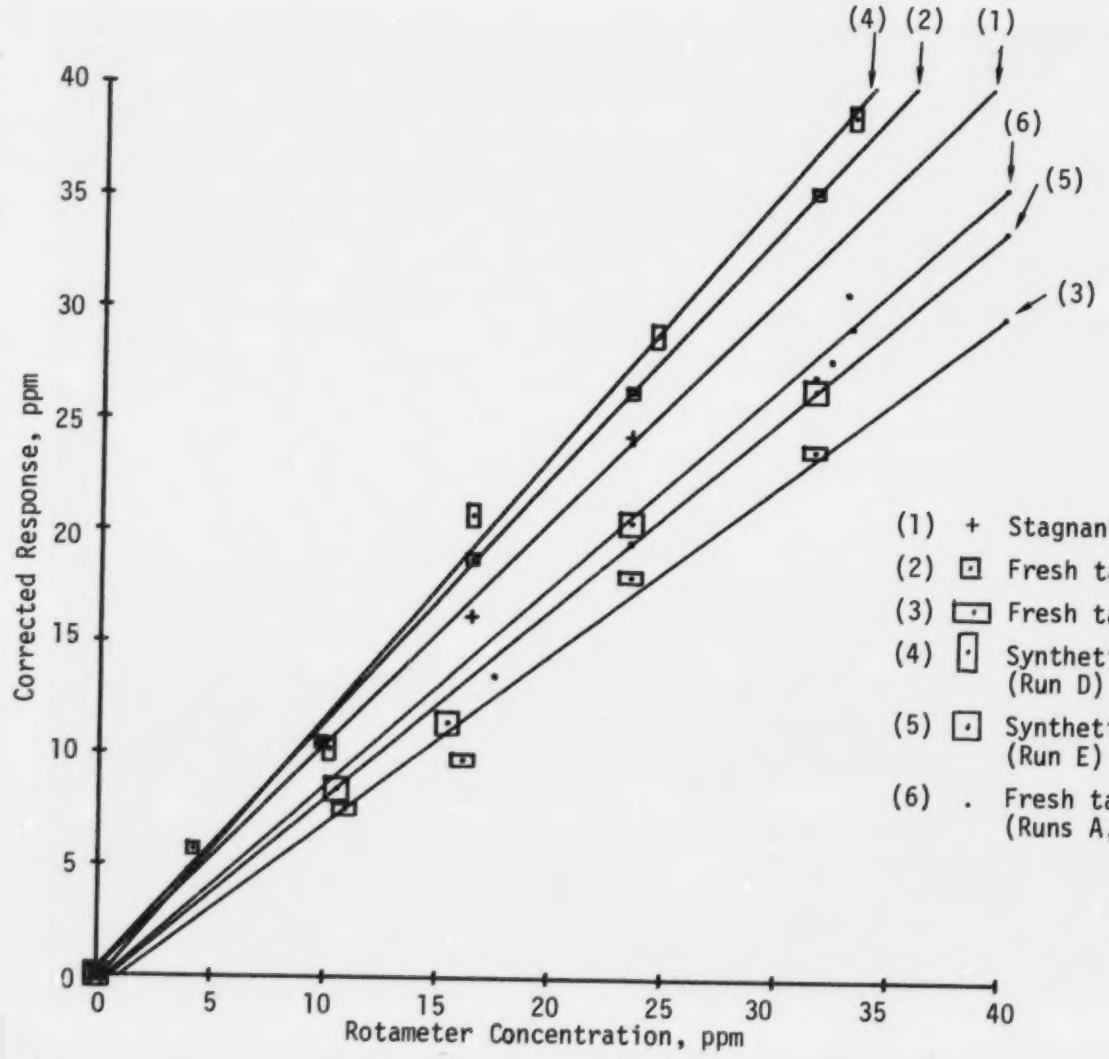

Figure 20. Effect of water type and temperature on Invalco response to DF-2.

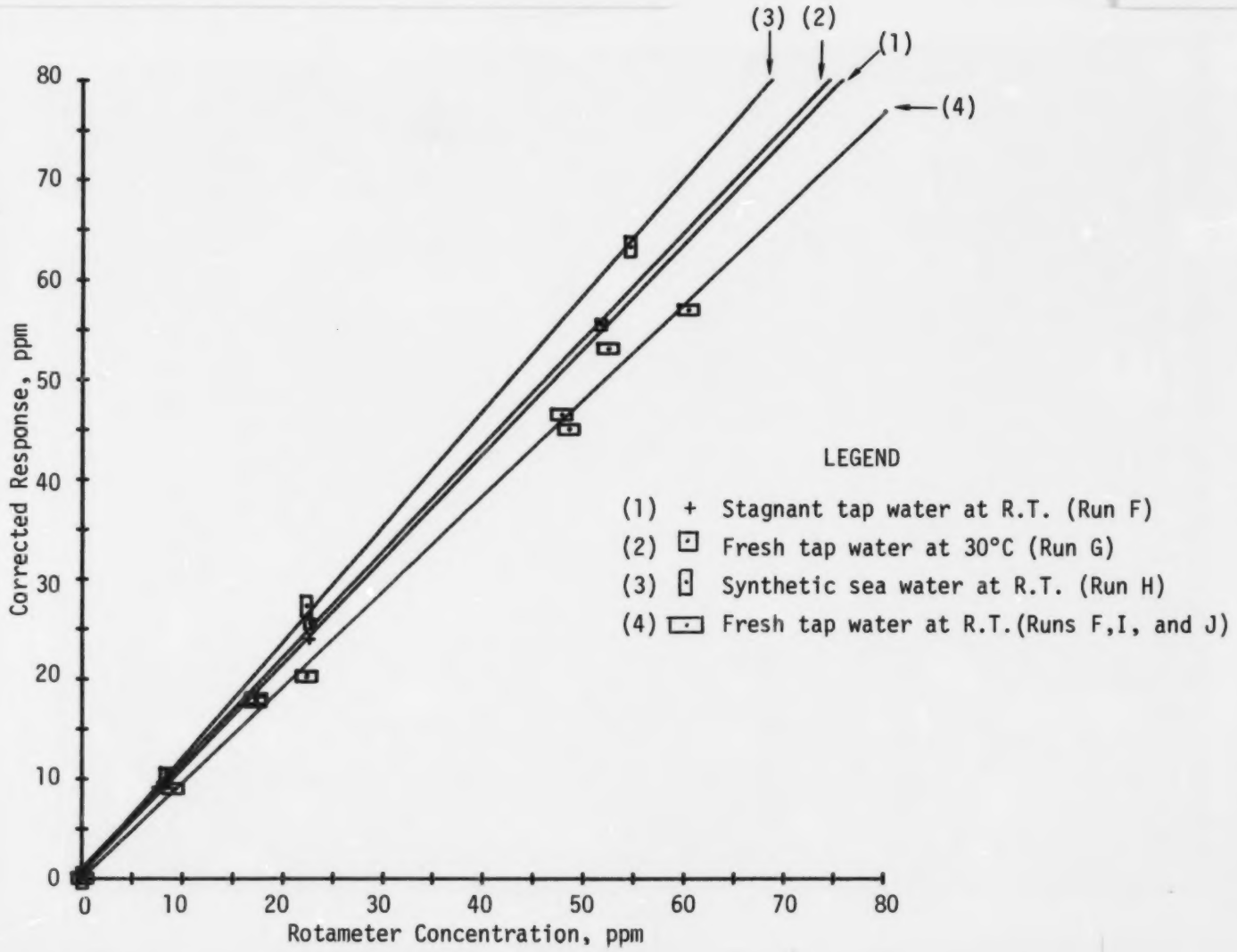

Figure 21. Effect of water type and temperature on Invalco response to Gulf crude oil.

TABLE 20. PRECISION OF INVALCO LINEAR-CURVE-FITTED DATA

Curve (No.)	DF-2 Correlation Coefficient	DF-2 Error (± %)	Gulf Crude Oil Correlation Coefficient	Gulf Crude Oil Error (± %)
(1)	0.9977	3.11	0.9971	3.28
(2)	0.9987	3.75	0.9989	2.69
(3)	0.9864	4.57	0.9994	1.22
(4)	0.9949	4.33	0.9951	3.94
(5)	0.9939	3.07	--	--
(6)	0.9736	5.77	--	--

Repeatability--A measure of the repeatability of the Invalco can be found in an examination of its responses to Gulf crude oil in fresh tap water at room temperature over a period of several days. The data are listed in Tables 13, 16, and 17. Since these data were obtained over several days under essentially the same experimental conditions, they provide a good measure of the Invalco repeatability. A plot of the three sets of data is shown in Figure 22. Agreement among the three linear curves, though relatively good, does show a disturbing and somewhat surprising change in sensitivity between curves (2) and (3). Apparently, the Invalco is subject to sudden shifts in sensitivity, thereby adversely affecting its repeatability.

Response Speed--The response speed of the Invalco was such that, within 15 to 30 seconds of the introduction of an additive to the flow stream, the Invalco would detect its presence. It would measure 90% of the response change, in general, within 60 seconds of additive introduction. Upon additive shutoff, the Invalco essentially reached background level in 30 seconds. These reaction times are, of course, as much a characteristic of the flow loop as of the detector.

Reliability--The first notable operational problem with the Invalco occurred about 2 months after its arrival. During a series of test runs in which the "CAUTION" limit was exceeded, it was observed that the wiping unit did not engage. The timer circuit board was removed and inspected. The back card support appeared to be askew, causing some measure of misalignment of the circuit board with the card edge connector. Following proper installation of the back support, the card was reinserted and proper operation resulted.

A second more serious problem with the Invalco involved a "zero shift" that continued to worsen during the testing program. When the flow loop was disengaged and clean tap water allowed to remain in the cell, the light transmitted through the cell began diminishing immediately, resulting in a greater than 50% transmittance loss in 72 hours, which would drop to less than 10% when

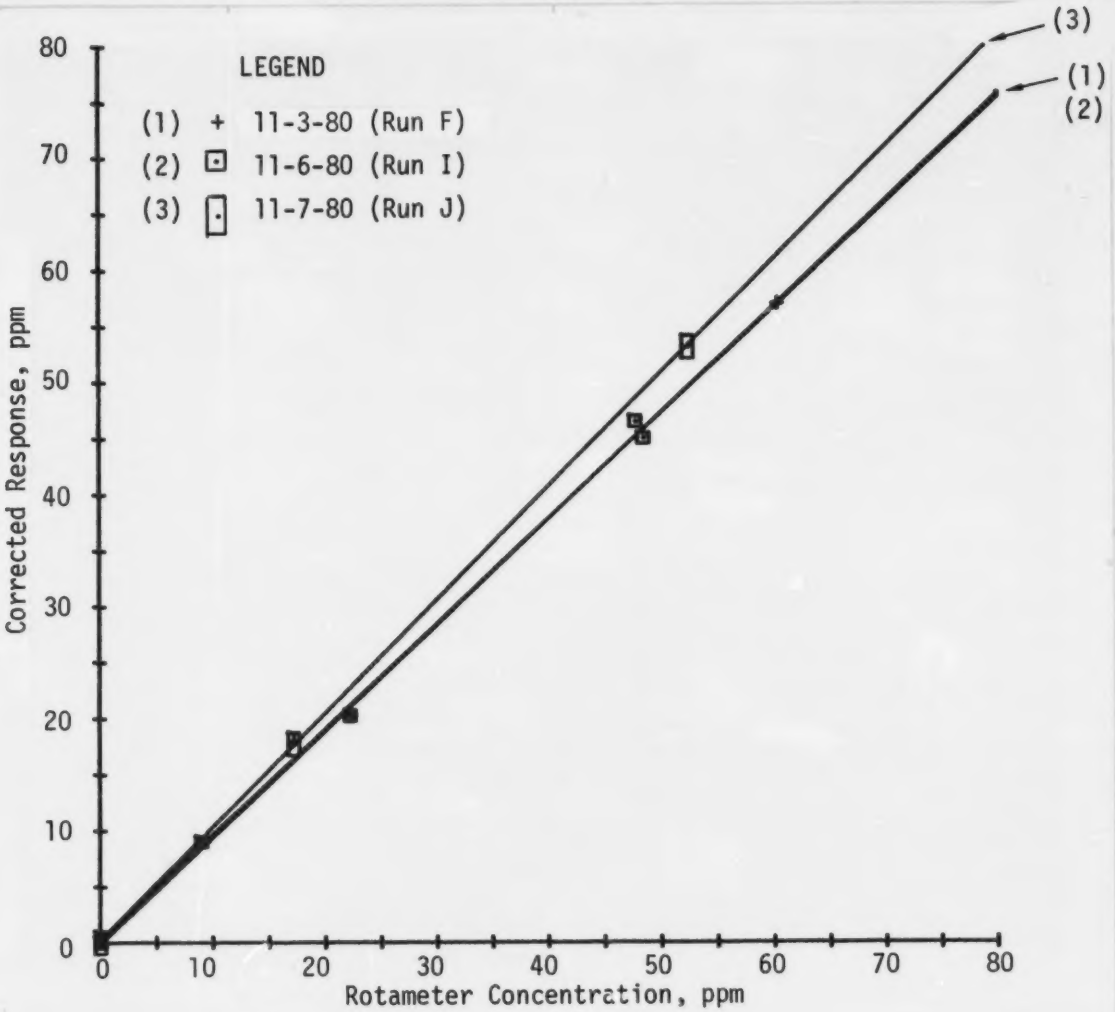

Figure 22. Effect of time on Invalco response to Gulf crude oil in fresh tap water at room temperature.

flow was re-engaged. To drop the loss to 1% to 2% FS often required 2 to 3 additional hours of constant flow. Allowing the cell to drain following flow loop shutdown worsened the problem. Since the flow loop was regularly shut down overnight as part of the standard operating procedure, readjustment of the Invalco amplifier balance (see this section, Calibrations, Detectors) was required to offset the transmittance loss. Over a 2-month period, the cumulative loss was approximately 30%. Unfortunately, when the amplifier balance pots would no longer respond to adjustment, the ultimate effect was a cumulative increase in background light absorbance, as witnessed by the Invalco indicated background response seen in Tables 6 through 18. Although continuous-flow operation, for which the Invalco was admittedly designed, may reduce this "zero-shift" tendency, it does not appear sufficient to preclude the same ultimate disposition.

Investigation of the source of the problem led to disassembly of the Invalco flow cell. The quartz cell was found scoured externally, rust-colored residues were found on the wiper assembly, and light source and detector assemblies were found not rigidly mounted. Tests showed that the latter optical system deficiencies were able to produce up to a 10% shift in readout. Remedial steps were taken to eliminate these problems and replacement parts were obtained from the vendor. However, the "zero-shift" problem remained.

Horiba--

The Horiba does a good job quantifying petroleum oil in water with aromatic hydrocarbons present. On average, the Horiba responds on a somewhat less than one-for-one basis to crude oil and aliphatic hydrocarbons, and on a somewhat greater than one-for-one basis to diesel fuel.

Interferents--Since the Horiba is based on the principle of solvent extraction with IR absorption at 3.4 to 3.5 micrometers, it should be sensitive to aliphatic hydrocarbons and various blends and mixtures to the extent that these compounds are contained in them. This is a valid assumption as demonstrated by the DF-2 data in Tables 6 through 10 and Gulf crude oil data in Tables 13 through 17. Also, the Horiba should ignore benzene and other aromatics to a great extent, and this is indicated by its response to benzene (1) in the presence of DF-2, as seen in the data in Tables 6 through 10, and (2) in the presence of Gulf crude, as seen in the data in Tables 13 through 16. Both sets of Horiba data show a minimal response to the presence of benzene, even in concentrations well over 100 ppm. The Horiba response to isooctane is substantial, of course, as shown by the data in Tables 6, 9, and 10. Also, the Horiba detects olive oil, as seen by the responses in Tables 11 and 18. Although olive oil is an olefin, the Horiba is responding to the saturated hydrocarbon portion of the fatty acid chain.

In addition, the data in Table 12 shows that detergent appears to have a negligible effect on the Horiba response. Detergent at a 10 ppm concentration level neither was detectable by itself nor did it produce a change, within experimental error, in the measured response to 50 ppm DF-2. However, the Horiba experienced the same slow return to background after DF-2 supply cutoff that the other detectors did in the presence of the detergent.

Sensitivity (Water and Temperature)--The Horiba sensitivity can be investigated by plotting its responses to DF-2 and Gulf crude oil. A plot of corrected response versus rotameter concentration for the Horiba/DF-2 data from Tables 6 through 10 has resulted in six linear curves and they are depicted in Figure 23. They show a Horiba response sensitivity to DF-2, on the average, of about 1.15:1. Figure 23 also shows the dependency of the Horiba/DF-2 response to water type and temperature. It would appear, from curves (2), (3), and (6), that the Horiba sensitivity to DF-2 is virtually independent of temperature in fresh water. One may argue that this conclusion is not an absolute certainty since the circuitous path the sample fluid has to follow within the Horiba flow loop (see Figure 11) may allow sufficient time for flow samples to thermally equilibrate to room temperature. However, this explanation does not appear satisfactory when the temperature dependency exhibited in the case of the Horiba responses in synthetic sea water, (4) and (5), is considered. This dependency translates to a 5% higher sensitivity to DF-2 at 30°C

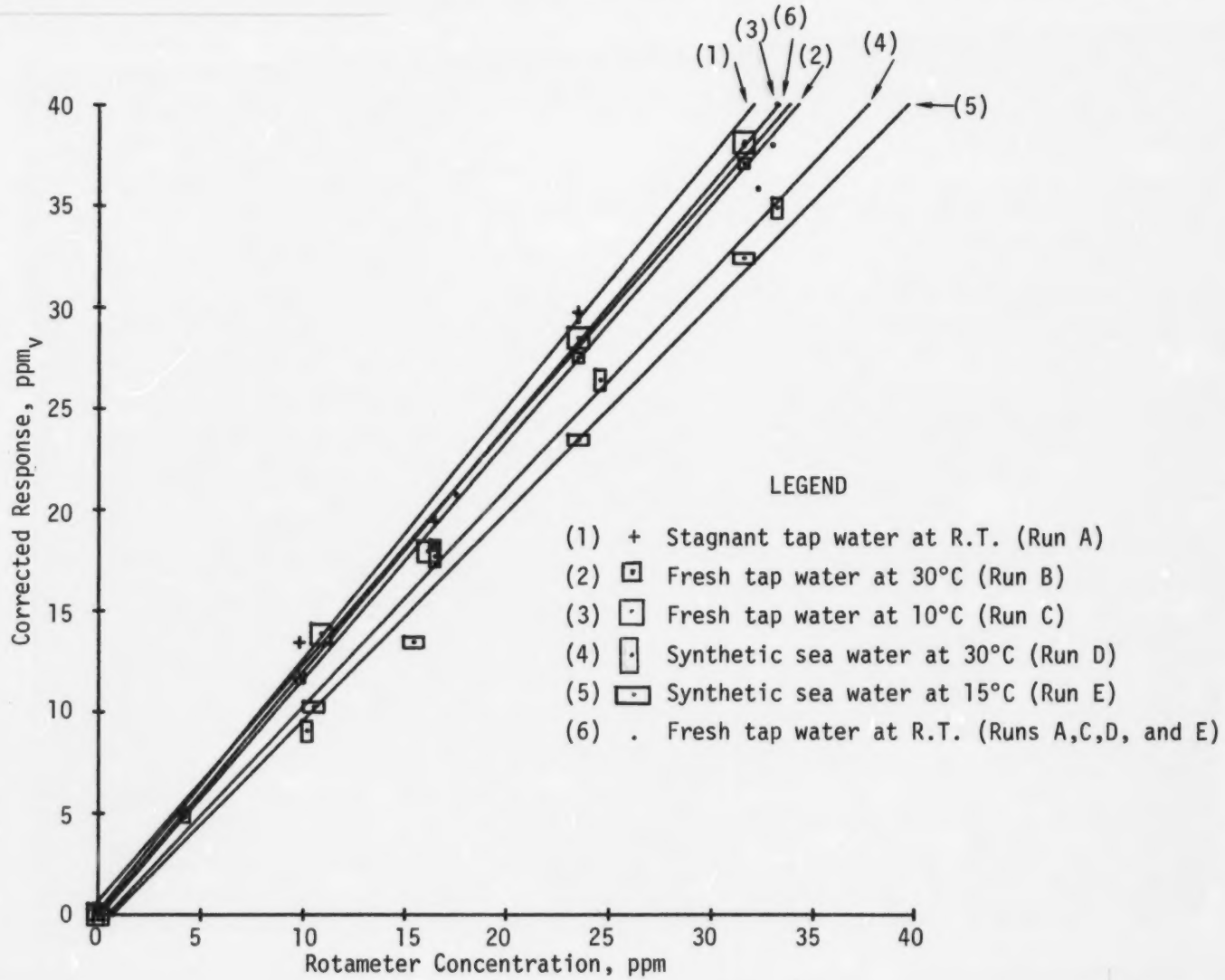

Figure 23. Effect of water type and temperature on Horiba response (without acid injection) to DF-2.

than at 15°C. The effect of dissolved solids in tap water (synthetic sea water) on Horiba response to DF-2 can be examined by comparing curves (2) and (4). At essentially the same temperature, the use of fresh tap water in place of synthetic sea water results in a 10% greater sensitivity. It is not believed that acid injection (not in use at this time) in the Horiba could reconcile this difference, since lowering the pH of the sample fluid to facilitate the solvent extraction may produce less of a sensitivity enhancement in sea water, a highly buffered solution, than in tap water.

A plot of corrected response versus rotameter concentration for the Horiba/Gulf crude oil data from Tables 13 through 16 has produced four linear curves and they are depicted in Figure 24. They exhibit an average response

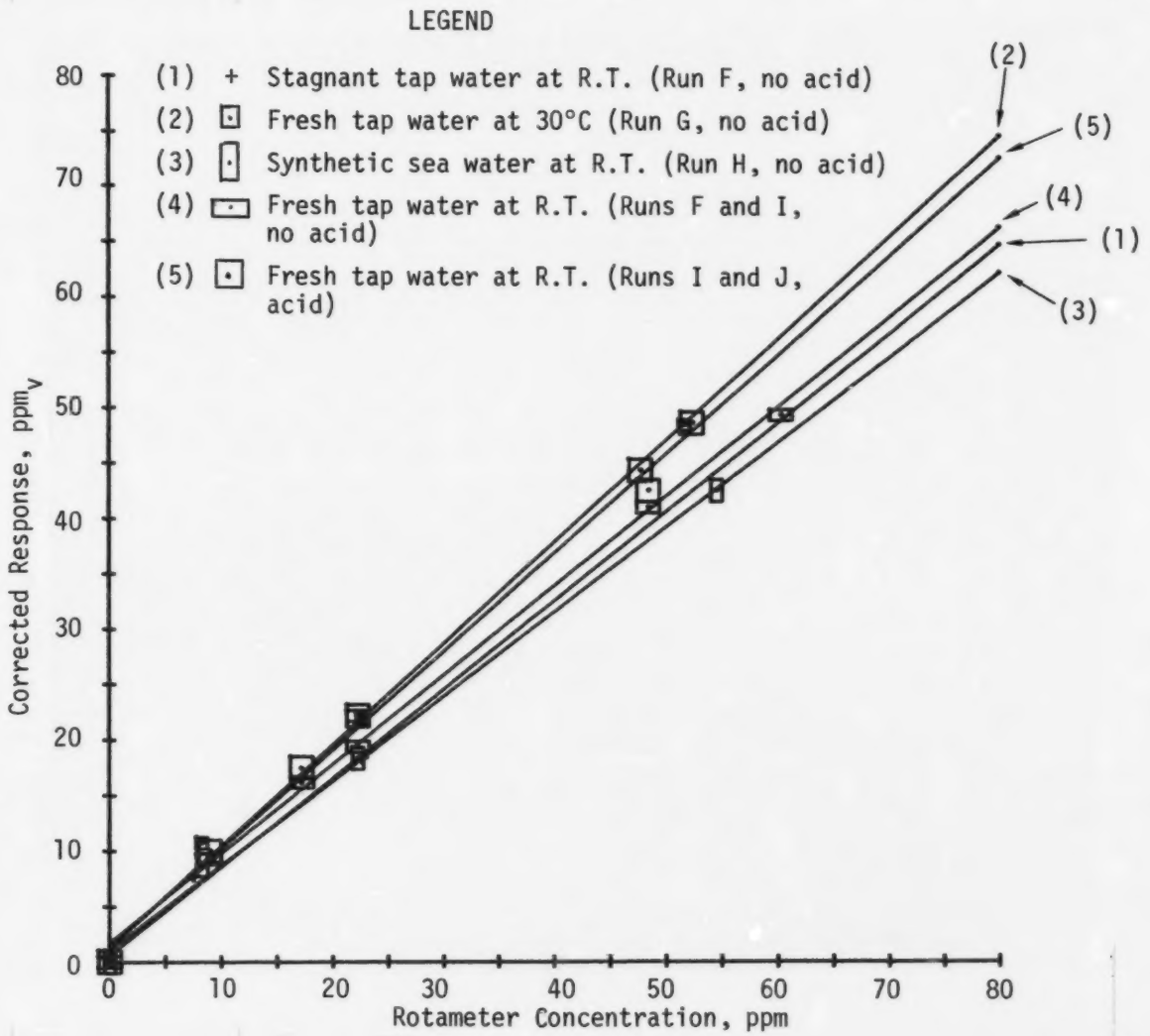

Figure 24. Effect of water type and temperature on Horiba response (with and without acid injection) to Gulf crude oil.

sensitivity to Gulf crude of about 0.85:1. Figure 24 also shows the dependency of the Horiba/Gulf crude response to water type and temperature. In comparing curves (2) and (4), it can be seen that the Horiba sensitivity to Gulf crude in fresh tap water at 30°C is about 15% greater than that at room temperature. The effect of dissolved solids in tap water (synthetic sea water) on Horiba response to Gulf crude can be judged by comparing curves (3) and (4). At essentially the same temperature, fresh tap water in place of synthetic sea water produces about a 7% greater sensitivity in the Horiba, quite similar to the results noted above with DF-2. Another item of note in Figure 24 is the difference between curves (4) and (5). The Horiba's use of acid injection into a sample stream of fresh tap water at room temperature increases the sensitivity by close to 10%. Although it is helpful to have the greater sensitivity, there are other considerations that must be taken into account. If the Horiba has equal repeatability with and without acid injection, then the practicality of a device that does not require periodic addition of acid is of great value in the multidetector monitoring system.

Linearity and Accuracy--The plots of Horiba responses to DF-2 and Gulf crude oil versus rotameter concentrations, in Figures 23 and 24, respectively, were accomplished by computer in accordance with a least-squares linear curve fit. This choice of curve-fitting, as with the data of the other devices, was selected because of the manufacturer's specifications for a linear detector output. The resultant linear curves appear to aptly describe the data. The corresponding correlation coefficients (coefficients of determination) resulting from the computer curve-fitting and the average error of the data used in the development of each curve are listed in Table 21. The average error of the data is a measure of the precision of the system generating the data. If systematic errors are eliminated (or compensated for by calibration), the average error of the data becomes a measure of the accuracy of the system. A minimum correlation coefficient of 0.995 is considered an indication of a good

TABLE 21. PRECISION OF HORIBA LINEAR-CURVE-FITTED DATA

Curve (No.)	DF-2		Gulf Crude Oil	
	Correlation Coefficient	Error (± %)	Correlation Coefficient	Error (± %)
(1)	0.9949	3.85	0.9900	5.82
(2)	0.9989	1.59	0.9960	5.21
(3)	0.9966	3.06	0.9969	4.65
(4)	0.9964	3.74	0.9939	3.15
(5)	0.9937	3.06	0.9959	3.21
(6)	0.9901	3.04	--	--

curve fit. The average error of the curve-fitted DF-2 data produced with the Horiba is ±3.06%, while that of the curve-fitted Gulf crude oil data is ±4.41%. These values are higher than the manufacturer-claimed accuracy of ±2% FS; however, it should be noted that the operational characteristics of both the flow loop and the detector contribute to the average error.

Repeatability--A measure of the repeatability of the Horiba can be found in an examination of its responses to Gulf crude oil in fresh water at room temperature over a period of days. The data are listed in Tables 13, 16, and 17. Since these data were obtained over several days under essentially the same experimental conditions, they provide a good measure of the Horiba repeatability. A plot of the three sets of data is shown in Figure 25. Run I

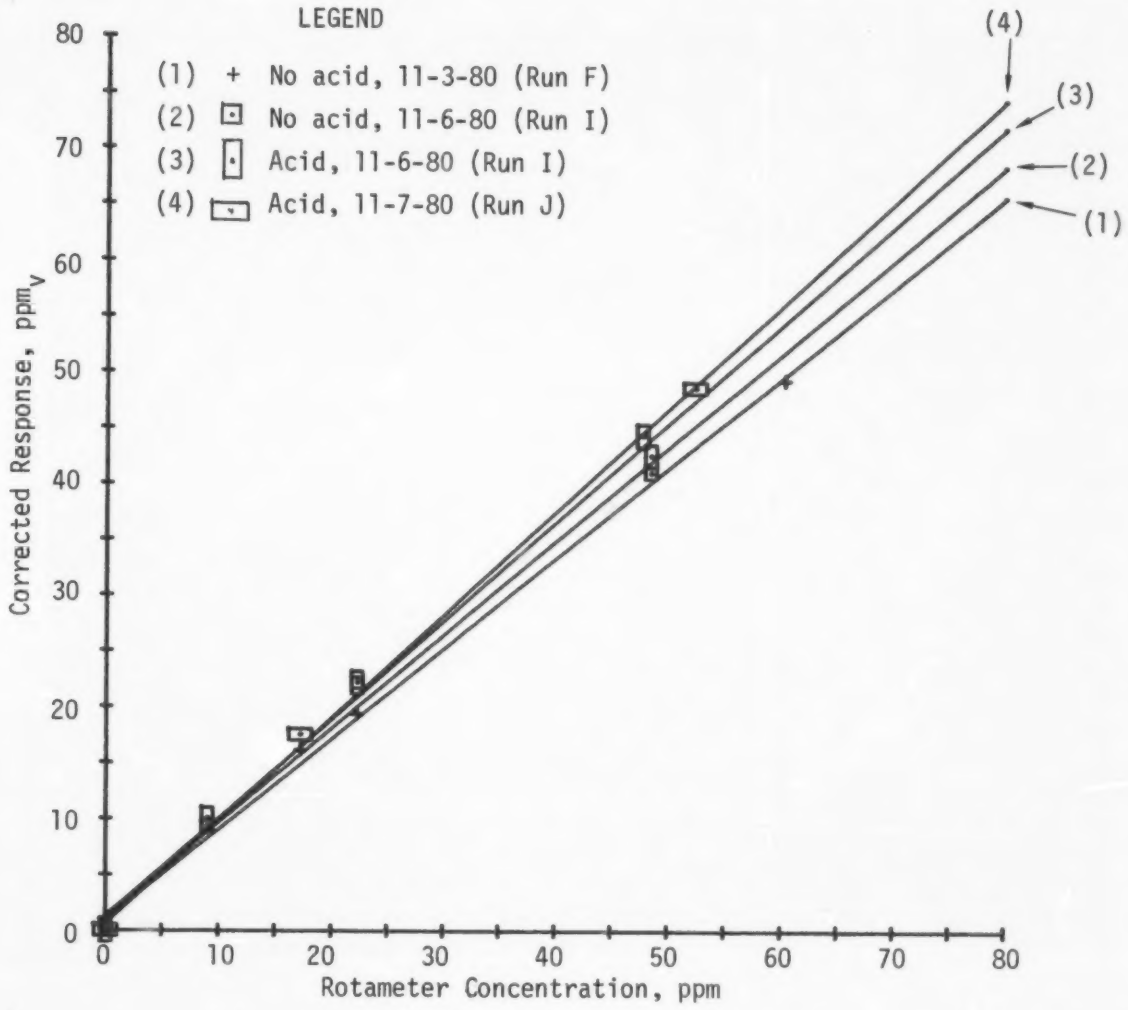

Figure 25. Effect of time and acid injection on Horiba response to Gulf crude oil in fresh tap water at room temperature.

was conducted both with and without acid injection, thus resulting in the production of four curves, two generated with acid and two without. The curves, both with and without acid injection, show an increasing bias with time in the sensitivity of the Horiba. Although any change is undesirable, an indication of decreasing sensitivity might be more plausible.

Response Speed--In the original pump module configuration the Horiba OCMA-25 would sense the presence of an additive in the flow stream in approximately 1¼ minutes. After the pump module modification (see this section, Calibrations, Detectors), the Horiba generally required 2½ minutes for an equivalent detection. To achieve 90% of the response change, the modified Horiba took an additional 5 minutes. Upon additive shutoff, the same Horiba reached essentially background level in about 5 minutes. These reaction times are, naturally, dependent on characteristics of the flow loop as well as the detector; however, most of the Horiba response lag is due to the device itself, as confirmed by the response times of the other detectors connected to the same flow loop.

Reliability--With respect to reliability, the Horiba OCMA-25 was described by a company spokesman as building "on the experience gained with the 32A to implement many improvements. The improvements are associated primarily with reducing the maintenance required by the analyzer system...".* This claim, along with the reported plan by Horiba to phase the OCMA-32A out of production within a year and replace it with the OCMA-25, prompted the investigator in mid-June (when delivery of the OCMA-32A, originally ordered, was delayed) to switch to the OCMA-25 for use in the current evaluative study. When the OCMA-25 was delivered in mid-September, it was equipped with a 0-20 ppm range (in contrast to the 0-200 ppm range originally ordered with the OCMA-32A) and two 10-liter tanks for pH adjuster fluid and zero water, which according to the instruction manual require filling every half week, as a rule. The OCMA-32A had no requirement for filling tanks such as these.

While it may be true that certain new features of the OCMA-25, such as an automatic calibration circuit, may have reduced the maintenance required, it also seems apparent that other changes, such as the fluid tanks, increased the maintenance demand. In some applications, periodic maintenance every few days would be prohibitive. However, the testing program results do indicate that although acid injection improves the Horiba OCMA-25 sensitivity, it apparently is not required for reliable operation. In addition, provision can be made for a field unit to automatically draw the zero fluid, required for calibration, from the sample stream when the multidetector system has determined that the sample stream is clean.

The only major problem with the operation of the Horiba was the "over-ranging" that occurred due to the 0-20 ppm range of the device. The device apparently can be provided by the factory with a range of 0-100 ppm. However, since information and hardware to accomplish this goal were not available, a plan to reverse the pump module and to correspondingly adjust the readout data was developed by the investigator and suggested to Horiba as an alternative. With their concurrence, the modification was made.

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* Letter from the Industrial Marketing Manager, Horiba Instruments, Inc., Irvine, California, June 1980.

It should be noted that despite a plethora of mechanical and electrical parts, the Horiba has not exhibited a single equipment failure during its operation at Rockwell EMSC. The device, securely housed in a sturdy metal frame, appears rugged enough for field use.

SECTION 6

SUGGESTED DESIGN AND DEVELOPMENT WORK

As a result of the information generated in the laboratory evaluation study, it is recommended that a subsequent effort be undertaken to develop a prototype multidetector petroleum oil-in-water monitoring system that will include the Sigrist Fluorescence Monitor Model FLJ and the Horiba OCMA-25 Oil Content Monitor. The Invalco D.O.W. Monitor is marginal for inclusion because of its general inability to discriminate between a known oil and selected interferents. About the only group of interferents that the Invalco does not respond to is water-soluble, nonaromatic organics, one example of which is methanol.

However, since three discriminating detectors are better than two, a limited review of the commercially available detectors (based on the original desk-top evaluation [see Appendix]) is suggested to identify a suitable substitute, i.e., a detector that utilizes UV absorption and has a high probability of discriminating better than the Invalco. If this search does identify a suitable substitute, the identified detector should be evaluated experimentally before inclusion in the multidetector system. If the search is unsuccessful and a determination is made to use the Invalco, then the source of the "zero-shift" problem must be found and eradicated.

In addition, it is recommended that the Sigrist response suppression by aliphatic hydrocarbons be investigated further so that a satisfactory resolution may be found. Lastly, the Horiba OCMA-25 should be an original 0-100 ppm range unit or a factory-converted 0-100 ppm range unit.

PRELIMINARY PROTOTYPE DESIGN

A preliminary design of the prototype multidetector petroleum oil-in-water monitoring system has been developed and includes a flow loop schematic and a data retrieval system for handling the data and computing the quantity of petroleum oil in water.

Flow Loop

The preliminary design of the flow loop for providing the necessary sampling system to assure taking a representative sample and distributing it appropriately to the selected detectors is depicted in Figure 26. The design includes a constant-velocity syringe pump, B, with a variable-rate drive so that known oil calibrations at a variety of stable concentration levels can be produced in the field. Calibrations will, therefore, be made with the clean sample stream as background. A properly enclosed syringe pump should be more

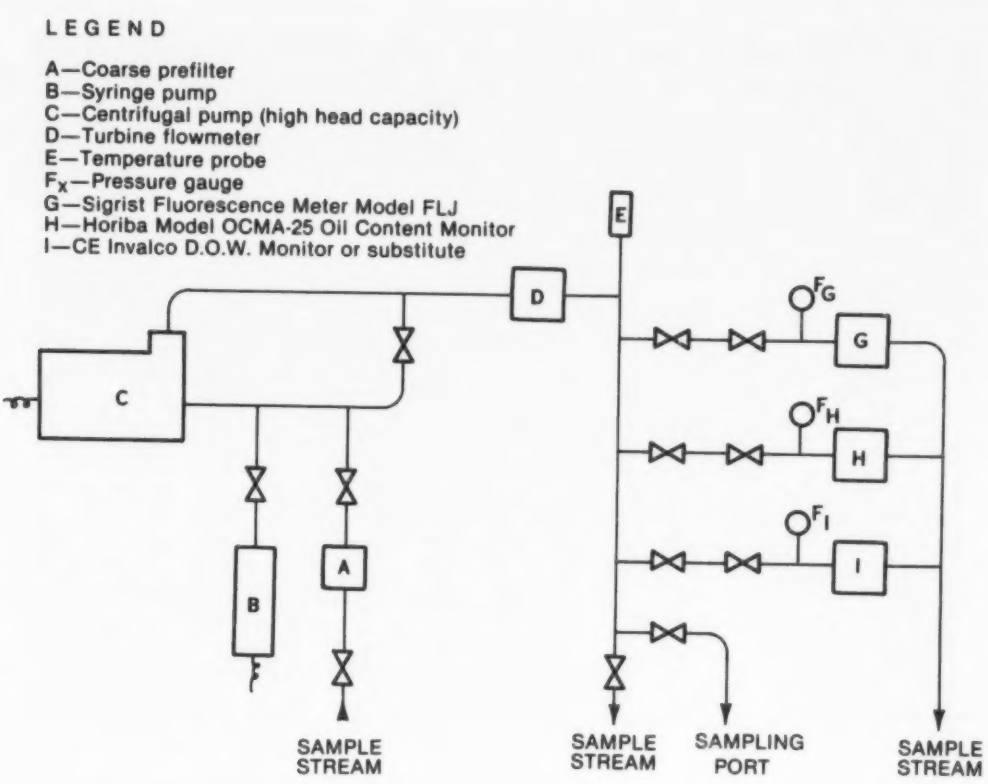

Figure 26. Conceptual flow loop design for prototype system.

ideally suited for rugged field use than the eductor system employed in the current evaluation. The syringe pump can be fabricated in-house or purchased from a commercial vendor. A centrifugal pump, C, will again drive the fluid stream forming a dispersion of known oil/interferents in water. Of course, it should be noted that there will be system limitations on the maximum pump height above, and distance from, the sample stream. Therefore, a centrifugal pump with a high head capacity will be required. A turbine flowmeter, D, will monitor the flowrate to the detectors. The turbine flowmeter can be alarmed for variations in flowrate of more than a fixed amount from a given setting. A temperature probe, E, will again provide a digital output suitable for minicomputer interfacing. The individual detector flow hookups will be similar to that employed in the present study, i.e., shutoff valves, metering valves, and pressure gauges for delivery of the proper manufacturer-specified flow to each detector.

Data Retrieval System

The outputs from the three detectors will be reduced by a minicomputer to provide a concentration value for the petroleum oil in water. This is to be accomplished by feeding the analog outputs of the two detectors, the Sigrist and the Invalco or its replacement, to a standard V/F converter (analog voltage to frequency converter), which converts the signals to a digital format. The

signals are then fed to a shift register to produce a real-time delay in them so that they can be matched up with the Horiba digital output as it becomes available. The matched signals are fed to an RS-232 interface, which converts the digital information into computer or assembly language, which is then used by a minicomputer to produce the concentration of petroleum oil in the sample stream.

Hardware--

A minicomputer considered acceptable for incorporation in the prototype multidetector system is the Radio Shack TRS-80, Model III, or its equivalent. It is a self-contained, desk-top unit that would require some form of weatherproofing or humidification for field use. Its basic 4 K memory package is easily expandable to 48K (which can be further increased with four 175K memory disk drives, although not required). The system also includes upper and lower case ability plus two-speed cassette operation, 500-baud and 1500-baud (for three times faster tape loading), a real-time clock, expanded "special" character set, printer/video routing, keyboard-controlled screen printing, repeating keys, and software for an RS-232 interface. Also available from Radio Shack and recommended for inclusion are an RS-232C Interface Board, a CTR-80A Cassette Recorder, and a Line Printer VI.

Software--

The software language used by the TRS-80, Model III, is BASIC. Since BASIC is generally considered preferable for use by personnel unsophisticated in computer programming techniques, a system employing such computer language should offer greater opportunities for use. The Model III BASIC programming offers multi-dimension arrays, comprehensive string variable handling, automatic line numbering, tracing, PEEK and POKE, call-up of machine language routines, printer commands, and 23 specific error codes.

Data Reduction--

It is anticipated that the software developed for the multidetector system will include a series of commands for the minicomputer to (1) tabulate the calibration response data obtained on a known oil, (2) develop an equation (by computer curve-fit) for each device correlating actual concentration to response concentration and temperature, (3) store the developed equations applicable to each detector in the computer memory for future reference, (4) tabulate response data from a sample stream containing unknown quantities of the known oil plus interferents, (5) compute a concentration of known oil corresponding to each detector's response and the stream temperature using the previously developed calibration equations, (6) search the three calculated concentration values for the lowest of these values (if all potential interferents are additive), and (7) report this lowest value as the concentration of the known oil. If the two lowest values or all three values are in agreement, the possibility is high that the reported concentration is the actual concentration. If the two lowest values are not in agreement, the reported concentration is equivalent to an upper limit on the actual concentration.

Table 6 provides a typical example of how the envisioned data reduction operation would work. To calibrate the multidetector system, the known oil, in this case DF-2, would be introduced into the sample stream at several concentrations. The minicomputer would then correlate the actual concentrations

of input DF-2 with measured responses. (If a second or third calibration set is done at different sample stream temperatures, by calibrating perhaps at different times of the day, the minicomputer can correlate actual concentrations with measured responses and temperature.) The computer would store the derived correlation equations for future use.

If a quantity of DF-2, 23.5 ppm, is present in the sample stream, and benzene, 117.2 ppm, is introduced later (see Table 6), the Horiba total corrected response climbs slightly (from 29.8 to 32.0 ppm) but the Sigrist response (at 0.82 ppm) ignores the benzene. Using the previously derived correlation equations, the minicomputer would calculate a value of DF-2 from the response for each device. In this case, a calculation for the Horiba might indicate a DF-2 concentration of 25.2 ppm, while the Sigrist would indicate 23.5 ppm of DF-2. (It is interesting to note the Invalco response more than quadrupled as a result of the benzene addition, not unexpectedly since it should respond to an aromatic hydrocarbon.) The computer would search the computed DF-2 concentrations for the lowest value. In this case, the Sigrist value of 23.5 ppm is flagged as the lower value (or lowest, if the Invalco readout is included) and would be reported by the computer as a maximum DF-2 concentration. The reason for not reporting this value as the actual DF-2 concentration is that the computer has no way of knowing whether the Sigrist and Horiba responses contain additive contributions from other interferents. However, in those cases where two or more of the integrated monitoring devices produce responses that, after minicomputer reduction, result in essentially the same calculated concentration for the known oil, this resultant concentration should be considered accurate since the probability of a group of interferents producing similar additive responses in two or more of the detectors is believed to be rather slim.

The data reduction procedure described above could also be utilized to determine the actual DF-2 concentration when both benzene and isooctane are introduced into the sample stream (see Table 6). Because of the quenching effect of the isooctane on the DF-2 fluorescence, observed by the Sigrist detector, suitable information on this phenomenon would have to be stored in the computer to allow it to compensate for this quenching effect. Data for this may be obtainable from the Horiba response which, as expected, does indicate the addition to the sample stream of aliphatic hydrocarbons such as isooctane.

PROTOTYPE DEVELOPMENT PROGRAM

A follow-on program is envisioned that will involve developing a full-scale prototype of the multidetector monitoring system and evaluating the detection system, first in the laboratory and then in full-scale field trails.

Laboratory Testing

Upon purchase of the selected instrumentation, the system will be assembled according to the approved preliminary prototype design. If a replacement detector for the Invalco is found, its performance will be evaluated under controlled laboratory conditions before inclusion, if merited, in the multidetector system. Also, an investigation to find a resolution of the Sigrist response suppression problem will be conducted. The computer hardware

and software will be integrated with the selected detectors and the prototype system will be checked for system integrity under laboratory conditions. The multidetector system will then be mounted on a skid or transportable frame and shipped to the EPA OHMSETT facility for full-scale field tests.

Field Testing

A demonstration test plan will be prepared. The test plan will include a description of those tests that will evaluate reliability, reproducibility, sensitivity, ruggedness, ease of operation, range, and effect of interferents. The prototype system will then be tested in accordance with the approved test plan at the EPA OHMSETT facility. All hardware will be delivered to the customer upon completion of the development program, together with an operation and maintenance manual. Copies of a complete set of working drawings including parts details and assembly drawings with a complete parts list will be provided.

APPENDIX

OIL MONITOR SURVEY

To determine the feasibility of developing a multidetector monitoring system for the continuous quantification of petroleum oil in water, a survey of commercially available oil monitors was conducted. This study, designated the Oil Monitor Survey, involved a desk-top analysis of currently available oil monitors and evaluation of their detection concepts, resulting in recommendation of several highest rated off-the-shelf oil monitors for inclusion in the detection system.

More than 40 manufacturers were contacted by telephone to identify oil-in-water monitoring devices that might qualify for the analytical evaluation. From the product literature and telecons, devices produced by 13 firms appeared worthy of evaluation. The names, addresses, and phone numbers of the manufacturers/suppliers of the selected devices are as follows:

Baird-Atomic, Inc.
125 Middlesex Turnpike
Bedford, MA 01730
(Dr. Linda Giering,
Mr. Herman Eldering)
(617) 276-6000

Biospherics Inc.
4928 Wyaconda Road
Rockville, MD 20852
(Mr. Gary Gottfried,
Ms. Suzanne Hughes)
(301) 770-7700

Bull & Roberts Inc.
785 Central Ave.
Murray Hill, NJ 07974
(Mr. Pete Magnani)
(201) 464-6500

C.E. Invalco
Combustion Engineering Inc.
1305 N. Louisville
P.O. Box 556
Tulsa, OK 74101
(Mr. Ron Russell)
(918) 932-5671)

Horiba Instruments, Inc.
1021 Duryea Ave.
Irvine, CA 92714
(Mr. Tim Scott,
Dr. Robert Gafford)
(714) 540-7874

Hyde Products, Inc.
(Bailey Effluent Monitor)
810 Sharon Dr.
Cleveland, OH 44145
(Mr. Brian Casey,
Mr. Ed Heidenreich)
(216) 871-4885

ITT Mackay Marine
(Conoflow Oilcon Monitor)
441 U.S. Highway #1
Elizabeth, NJ 07202
(Mr. Harry Smith)
(201) 527-0300

Keene Corporation
Fluid Handling Division
P.O. Box 250
Greeneville, TN 37743
(Mr. Harold McCartney) (615) 638-8156

Facet Enterprises, Inc.
Industrial Division
P.O. Box 50096
Tulsa, OK 74150
(Mr. Don Conley,
Mr. Bruce Teale)
(918) 939-5451

Gubelin Industries Inc.
(Sigrist Fluorescence Meter)
45 Kenisco Dr.
Mount Kisco, NY 10549
(Mr. Stephan Hangartner)
(914) 241-0130

Separation and Recovery Systems (SRS)
1733 Kaiser Ave.
Irvine, CA 92714
(Mr. Justin Branson)
(714) 979-8860

Teledyne Analytical Instruments
333 West Mission Dr.
San Gabriel, CA 91776
(Mr. Carl Jones, Mr. Dwayne Gates)
(213) 576-1633

Turner Designs
2247 Old Middlefield Way
Mountain View, CA 94043
(Mr. George Turner)
(415) 965-9800

The manufacturers whose devices did not qualify are listed in Table A-1, along with reasons for rejection. Manufacturers of nondomestic oil-in-water monitoring instrumentation are included in Table A-2. These nondomestic devices are not commercially available in this country, and therefore they were not analytically evaluated. Technical information deemed pertinent to the evaluation of the 13 devices was obtained and tabulated with respect to 25 technical specifications and qualifications, and the data are located in Tables A-3, A-4, and A-5.

The evaluation was accomplished by applying to each specification or qualification a factor that related the importance of that particular parameter to the features desired in the final product. Thus, maximum rating factors were assigned to each particular parameter and then each device was rated in accordance with criteria established to reflect differences in the various devices. The rating criteria can be found in Table A-6. As a result, product evaluation ratings were determined for the devices and are listed in Table A-7.

In an attempt to limit the number of recommended devices on technical rather than strictly arbitrary grounds, the devices were grouped, as can be seen in Table A-7, according to their principles of operation, which can be correlated to some extent to their presumed capability to measure free and/or dissolved oil (see Table A-3). The top-rated device for each basic principle of operation would then be selected for the prototype system. What this determination of a device's capability lacks in objectivity, it gains in the rationale that if one device (namely, the top-rated one) from each principle of operation category is incorporated in the multidetector petroleum oil monitoring system, the detection system stands a better chance of quantifying the oil through detection of its major components than it would if all the top-rated devices were to have come from one category. Since some components of petroleum oil remain insoluble in water while other components dissolve, the former, consisting mainly of paraffins (aliphatic and naphthenic hydrocarbons), can be detected by light-scattering and solvent extraction apparatuses while the latter, generally comprised of aromatic hydrocarbons and organic compounds,

TABLE A-1. MANUFACTURERS CONTACTED FOR PRODUCT INFORMATION
(THESE DEVICES WERE NOT ANALYTICALLY EVALUATED)

Manufacturer	Instrument	Reason for Rejection
Astro Ecology P.O. Box 58159 Houston, TX 77058 (Darryl Hazlett) (713) 332-2484	Process TC/TOC Analyzers Series 1800	Response not real time and chemical solutions must be periodically maintained.
Bailey Meter Co. Lim. 205 Brunswick Blvd. Pointe-Claire, Quebec H9R 1A5 Canada (Max Joubert, Jim Sterling) (514) 697-6770	Effluent Monitor Type OT312	No organization in USA or Canada currently involved in marketing/service of device. (A later contact located a distributor in the USA, Hyde Products, Inc.)
Beckman Instruments Advanced Technology Operations 1630 S. State College Blvd. Anaheim, CA 92806 (Paul Chase, John Burgess) (714) 634-4343	Automatic Real-Time Shipboard Oil-in-Water Monitor	Not commercially available.
Chemtrix 163 SW Freeman Ave. Hillsboro, OR 97123 (Bill Nelson) (503) 648-0762	--	No device commercially available.
Curtis Le-Vantine 18225 Rancho St. Tarzana, CA 91356 (Allan LeVantine) (213) 987-1928	--	No device commercially available.
Endress & Hauser 2350 Endress Place Greenwood, IN 46142 (Loretta Storm) (317) 535-7138	Interface Detector Series DC111	Does not quantify oil in water.

(continued)

TABLE A-1 (Continued)

Manufacturer	Instrument	Reason for Rejection
Enviro Control Inc. 960 Thompson Ave. Rockville, MD 20852 (Don MacArthur) (301) 468-2500	--	No device commercially available.
General Electric Environmental Control Division Philadelphia, PA (Tom Fagan) (215) 962-3491	--	No device commercially available.
Hach Chemical Co. Loveland, CO (Frank Kabot) (303) 669-3050	--	No device commercially available.
Baker Oil Tool Hallikainen Inst. Div. Rep: TOTCO Glendale, CA (Al Manning) (213) 245-7411	--	No device commercially available.
Intex 6935 Wisconsin Ave. Chevy Chase, MD 20015 (Norm Somerville, Ann Kelly) (301) 654-4550	Oiltect II	Individual batch analyzer.
Ionics Inc. 65 Grove St. Watertown, MA 02172 (Bruce Thayer) (617) 926-2000	M-82 Organic Contamination Monitor	Not real time, carrier gas cylinder(s) required, high temperature furnace, mechanical sample injection valve, and device measures all organics.
ITT, Barton Inst. Div. 900 S. Turnbull Cyn. City of Industry, CA 91749 (Bill Gosma) (213) 961-2547	Net Oil Computer Model 1200	Used to monitor oil and water in secondary recovery methods, i.e., 2% to 98% oil-in-water.

(continued)

TABLE A-1 (Continued)

Manufacturer	Instrument	Reason for Rejection
Liquidometer Corp. Naugatuck, CT (Russ Kerr) (203) 729-5253	(Name of device unknown)	Does not quantify oil in water.
Lockwood & McLorie P.O. Box 113 Horsham, PA 19044 (James Copeland) (215) 675-8718	Liquid Sampling System	Does not quantify oil in water.
Marine Electric Railway Products 166 National Rd. Edison, NJ 08817 (Charlotte Reilly, Gil Haring) (201) 287-2810	Oil-in-Water Detector	Monitors input to oily water separators, i.e., oil concentrations approaching 3000 ppm.
Marine Moisture Control 449 Sheridan Blvd. Inwood, LI, NY 11696 (William Henry) (212) 327-3430	Sonic Slop Tank Oil Detection System	Does not quantify oil in water; determines interface.
McNab Inc. 20 N. MacQuesten Pkwy. Mount Vernon, NY 10550 (John Grimes) (914) 699-1616	--	No device commercially available.
National Marine Service 827 Hanley Industrial Court St. Louis, MO 63144 (Dewey Bitney) (314) 968-4770	Bilgemaster I	Does not quantify oil in water.
Oceanography Int'l 512 West Loop College Sta., TX 77840 (Keith Egan) (713) 693-1711	TOC Analyzer	Individual batch analyzer.

(continued)

TABLE A-1 (Continued)

Manufacturer	Instrument	Reason for Rejection
Procedyne Corp. 221 Somerset St. New Brunswick, NJ 08903 (H.K. Staffin) (201) 249-8347	--	No longer handles oil-in-water monitoring devices.
Rambie Inc. 1100 E. Airport Fwy. Irving, TX 75061 (Guy Rambie, Jr.) (214) 438-6909	Scanning Oil Sensor or Oil Spotter	Does not quantify oil; monitors oil sheen on water.
Research Appliance Co. (RAC) Route 8 Gibsonia, PA 15044 (Wayne Baker) (412) 443-5935	--	No longer handles water-monitoring instruments.
Royco Instruments 141 Jefferson Dr. Menlo Park, CA 94025 (Richard Hood) (415) 325-7811	Particle Counter for Liquid Analysis Model 345	As presently constituted, does not quantify oil in water.
Seismograph Service P.O. Box 1590 Tulsa, OK 74102 (Lloyd Walker) (918) 627-3330	TOC Analyzer Series 2610	Not real time, acid reagent, cooling water, and reactant gas cylinder required, and high temperature furnace.
Technicon Instruments Corp. Industrial Systems Div. Tarrytown, NY 10591 (Barry Grusko) (914) 631-8000	Carbon Analyzer-101 (Monitor IV)	Not real time, and chemical solutions must be periodically maintained.
Texas Instruments Dallas, TX (Lloyd Bartling) (713) 491-5115	--	No device commercially available.

(continued)

TABLE A-1 (Continued)

Manufacturer	Instrument	Reason for Rejection
Uniloc 2400 Barranca Rd. Irvine, CA 92714 (Curtis Tom) (714) 546-8700	--	No device commercially available.
Velcon Filters Inc. 1750 Rogers Ave. San Jose, CA 95112 (Bob Marting) (408) 298-6525	--	No device commercially available.
Wright & Wright P.O. Box A Oak Bluffs, MA 02557 (Judy McClelland) (617) 693-2608	Infrared Oil Film Monitor Model C250	Does not quantify oil in water; monitors oil sheen on water.

TABLE A-2. NONDOMESTIC OIL-IN-WATER MONITORING INSTRUMENTATION*

Company Name	Instrument Designation	Operating Principle	Range (ppm)
AEG Telefunken Marine Division (and SLO, Finland)	OILI	Infrared Absorption without solvent extraction	0-10,000
Salen & Wicander, AB	SALWICO Oil Pollution Monitor, Models SOP, SOC, and BOM	Light Reflectance and Gas Evaporation from Oil-Absorbing Tape	0-200 0-1000
S.E.R.E.S.	DRUR	Visible light transmission	0-50 to 0-10,000
Shimadzu Seisakusho, Limited	ET-15B, ET-20	Ultrasonic Emulsification and Turbidity Measurement	0-15, 0-100
TOEI Electronics Co. Ltd.	Bilge Monitor	Infrared Scattering and Turbidity Transmission	0-100
Tamatake-Honeywell Co. Ltd.	BTP-400 Ballast BTP-300 Bilge	Turbidity	0-300, 0-1000 0-120

* These devices are not commercially available in the USA and therefore they were not analytically evaluated.

TABLE A-3. OIL-IN-WATER MONITORS - GENERAL SPECIFICATIONS

Instrument	Principle of Operation	Oil Form	Dimensions/ Weight	Rugged	Solid State	Modularized Components	Setup Ease	Water & Salt Spray Resistance	Warmup Time	Sample Flowrate	Pri e/ Delivery
Horiba Model OCMA-32A Oil Content Monitor	Solvent-Extraction & Infrared Absorption	Dispersed & (Dissolved)	14"x18"x30" (X2)/226 lbs	Yes	Yes	Yes	4 hrs	NEMA 4	60 mins	.2 to .4 gpm (nom: 1/4 gpm)	$8300 $10,800(AIC) $11,300 (rcdr) 4-8 wks del.
CE Invalco DOW Monitor	UV Absorption (ratio to visible)	Dissolved & (Dispersed)	11"x19"x24"/ 150 lbs	Yes	Yes	Yes	4-6 hrs	NEMA 3R (weathertight) NEMA 7 (explosion-proof)	15 mins	.1 to 1 gpm	$5200 (NEMA 4) $6500 (NEMA 7) 8 wks del.
Biospherics Oil Sentry	Forward light scatter and transmittance	Dispersed	13½"x10½"x 8½ 20"x6½"x4"/ 35 lbs	Yes	Yes	Yes	3-4 hrs	NEMA 4	5 mins	Up to 10 gpm	$4500 $4950 (recorder) 6-8 wks del.
Bull & Roberts Aqualert Model 240	UV Absorption (ratio to visible)	Dissolved & (Dispersed)	11"x14"x6"/ 20 lbs 20"x20"x8"/ 15 lbs	Yes	Yes	Yes	2-4 hrs	Weathertight NEMA 4 NEMA 7	30 mins	Up to 30 gpm	$4500 (Std) $5500 (NEMA 4) $6800 (NEMA 7) 3 wks del.
Baird-Atomic Petrolarm with Sample Conditioning Module	UV Fluorescence	Dissolved & Dispersed	20"x20"x8" (X2)/150 lbs	Yes	Yes	Yes	2 hrs	NEMA 4	20 mins	.1 to .5 gpm	$7600 $8400 (recorder) 5 mos del.
Facet Fluid Analyzer Mk 1	Near-Infrared Absorption	Dispersed	20"x10"x20" (X2)/185 lbs	Yes	Yes	Yes	1-2 hrs	NEMA 3R	30 mins	Up to 10 gpm	$6000 10 wks del.
Teledyne 661R Oil-in-Water Analyzer System with Local Meter and Relays	UV Absorption (ratio to visible)	Dissolved & (Dispersed)	68"x40"x24"/ 240 lbs	Yes	Yes	Yes	1-2 days (factory engineer)	NEMA 12 (Weatherproof) NEMA 7	120 mins.	1 gpm	$9000 $12,500 (NEMA 7, 660C) 3-4 mos del.
Sigrist Fluorescence Meter Model FLJ	UV Fluorescence (ratio to reference)	Dissolved & Dispersed	24"x12"x24"/ 175 lbs	Yes	Yes	Yes	1-2 days (factory engineer)	NEMA 3R	15-20 mins	1.1 to 1.9 gpm	$8250 $9050 (rcdr) $10,450 (failsafe) 8 wks del.
Keene Purity Monitor Model 861-W-1161-RS (R = optional recorder)	Forward light scatter and transmittance	Dispersed	22½"x20"x 8-3/4"/80 lbs 10½"x4" dia/ 40 lbs	Yes	Yes	No, Soldered Connections	1 hr	NEMA 4	5 mins	Up to 600 gpm	$6500 $7000 (recorder) 8 wks del.
ITT Conoflow Bilge Oilcon Monitor	Angular light scatter and transmittance (near-IR monochromatic laser light)	Dispersed	8"x6"x10"/ 10-20 lbs 6"x5" (dia)/ 5-10 lbs	Yes	Yes	Yes	5 hrs	Drip-proof	30 mins	Over 2.2 gpm	$15,000 $16,500 (recorder) 3 mos del.
Separation and Recovery Systems (SRS) Oil Content Alarm (OCA-1) with Homogenizer	Forward light scatter and transmittance	Dispersed	10"x10"x6"/ 18 lbs 6"x12"x6"/ 20 lbs	Yes	Yes	Yes	4 hrs	NEMA 4	< 1 min	Up to 20 gpm	$3900 $4550 (recorder) 4 wks del.
Bailey Effluent Monitor Type OTM with SCM	UV Fluorescence	Dissolved & Dispersed	23" x 17" x 15"/70 lbs 10" x6" (dia)/ 20 lbs	Yes	Yes	Yes	1 day (factory engineer)	NEMA 4	30 mins	0.5 to 2 gpm	$10,700 $12,950 (rcdr), 8 wks delivery
Turner Designs Field Fluorometer Model 10-005	UV Fluorescence	Dissolved & Dispersed	8" x 21" x 12"/32 lbs	Yes	Yes	No, Soldered Connections	1 hr	Water-resistant	5 mins	up to 5 gpm	$6000 $6800 (rcdr) 8 wks del.

TABLE A-4. OIL-IN-WATER MONITORS - OPERATING SPECIFICATIONS

Instrument	Temperature Range	Concentration Range	Accuracy	Response Speed (90% of Δ)	Remote Readout Output
Horiba Model OCMA-32A Oil Content Monitor	36-113 F (ambient) 36-95 F (sample)	0-20, 0-120, 0-200, 0-1000 ppm	±2% F.S.	< 45 secs	0-1 VDC, 4-20 maDC
CE Invalco DOW Monitor	40-150 F (ambient) 40-140 F (sample)	0-150 ppm	±5% F.S.	< 1 sec	4-20 maDC
Biospherics Oil Sentry	34-158 F (ambient and sample)	0-30, 0-150 ppm (operator selectable)	±2% F.S.	< 8 secs (Adj. alarm delay)	0-1 VDC or 4-20 maDC
Bull & Roberts Aqualert Model 240	32-125 F (ambient and sample)	0-100 ppm	±5% F.S.	< 2 secs	0-5 VDC, 0-5 maDC
Baird-Atomic Petrolarm with Sample Conditioning Module	32-130 F (ambient) 28-200 F (sample)	0-20, 0-200 ppm (0-315 ppm has been used successfully)	±5% F.S. or ±2 ppm	< 10 secs	0-10 VDC
Facet Fluid Analyzer Mk 1	40-150 F (ambient) 32-150 F (sample)	0-100 ppm	±1 ppm	< 2 secs	4-20 maDC
Teledyne 661R Oil-in-Water Analyzer System with Local Meter and Relays	32-125 F (ambient) 32-140 F (sample)	0-100, 0-150 ppm	±2% F.S. (with same oil calibration)	< 30 secs	mvDC (customer specified)
Sigrist Fluorescence Meter Model FLJ	14-122 F (ambient) 32-120 F (sample)	0-10 up to 0-1000 ppm (customer selectable)	±2% F.S.	< 15 secs	mvDC (customer specified)
Keene Purity Monitor Model 861-W-1161-RS (R = optional recorder)	-13-185 F (ambient) 32-185 F (sample)	0-10, 0-20, 0-100, 0-200 ppm	±1 ppm	< 1 sec (5-sec. alarm delay)	0-5 VDC
ITT Conoflow Bilge Oilcon Monitor	32-131 F (ambient) 41-158 F (sample)	0-20, 0-120 ppm	±20% F.S. or ±10 ppm (whichever is greater)	< 1 sec (1-2 sec. alarm delay)	0-20 ma, 4-20 ma
Separation and Recovery Systems (SRS) Oil Content Alarm (OCA-1) with Homogenizer	34-140 F (ambient and sample)	0-100 ppm	±5% F.S.	< 1 sec	0-10 VDC
Bailey Effluent Monitor Type OT3M w/SCM	50-140 F (ambient) 32-104 F (sample)	0-100+ ppm	±2% F.S.	< 1 sec	4-20 maDC
Turner Designs Field Fluorometer Model 10-005	32-122 F (ambient and sample)	0-50 ppm 0-100 ppm (with checking)	±2% F.S. (with good standard)	< 2 secs	0-5 VDC (analog output with range) Digital output (TTL compatible)

TABLE A-5. OIL-IN-WATER MONITORS - SPECIAL QUALIFICATIONS

Instrument	Special Circuitry	Self-Calibrating	Automatic Self-Cleaning	Zero Adjustable	Nonlevel Operable	Vibration Insensitive	Interference Avoidance	Alarm Features	Optional Equipment
Horiba Model OCMA-32A Oil Content Monitor	Filter alarm, calib.failure alarm (AIC), plus shutdown	Yes (option, AIC-101)	No (shuts down)	Yes	Yes	Yes	Suspended solids Air bubbles Oil droplet size Water color Temperature	Hi-adj. DPDT-5 amp (remote alarm check)	30-day strip chart recorder Calibration zero-span measurement (AIC-101)
CE Invalco DOW Monitor	Checkout-Failsafe	Yes, electrical (acrylic plastic)	Yes (cell periodically wiped)	Yes	Yes	Yes	Suspended solids Water color	Lo & hi-adj. SPDT-3 amp (3 lights)	(30-day strip chart recorder)*
Biospherics Oil Sentry	Checkout (lamp) (span) (zero) - Failsafe	No	Yes (cell periodically wiped)	Yes	Yes	Yes	Water color Source drift Temperature Suspended solids	Hi-adj. (for each range) DPDT-2 amp (at 110 VAC)	30-day strip chart recorder
Bull & Roberts Aqualert Model 240	Checkout - Failsafe	Yes, electrical	Yes, steam lines must be provided (8-hr cycle)	Yes	Yes	Yes	Air bubbles Scale, dust, dirt Source drift	Lo or hi-adj. 3PDT-3 amp	L&N 30-day strip chart recorder
Baird-Atomic Petrolarm with Sampling Conditioning Module	Checkout - Failsafe	Yes, electrical (quartz rod)	Yes, air curtain	Yes	Yes, 22.5°	Yes	Air bubbles Particulates	Two hi SPDT-3 amp	30-day strip chart recorder (Sample conditioning module)
Facet Fluid Analyzer Mk 1	Checkout - Failsafe	No	Yes, sample flow (2-month cleanout)	Yes	Yes	Yes	Air bubbles	Two hi-adj. D PDT-10 amp	(30-day strip chart recorder)*
Teledyne 661R Oil-in-Water Analyzer System with Local Meter & Relays	Checkout (zero)	No	Yes, valved air supply	Yes, automatic re-zero	Yes, 15°	No	Suspended solids Air bubbles Oil droplet size Source drift Temperature	Lo and/or hi-adj. SPDT-5 amp (at 115 VAC)	L&N 30-day strip chart recorder (Local meter and relays)
Sigrist Fluorescence Meter Model FLJ	Checkout/ Failsafe (option)	Yes, system measured against reference	Not necessary (free-fall)	Yes	Yes	Yes	Suspended solids Air bubbles Source drift Temperature	Lo and/or hi-adj. Microswitches .2 amp (at 220 VAC)	90-day strip chart recorder (speed = 3 cm/hr) Checkout/Failsafe circuit
Keene Purity Monitor Model 861-W-1161-RS	Checkout/ Failsafe	Yes, electrical including cell	No	Yes	Yes	Yes	Water color Source drift	Hi-adj.	30-day strip chart recorder
ITT Conoflow Bilge Oilcon Monitor	Checkout - Failsafe	No	Yes, continuous window flush	Yes	Yes, 22.5°	Yes	Suspended solids	Two hi-adj.	30-day strip chart recorder
Separation & Recovery Systems (SRE) Oil Content Alarm (OCA-1) with Homogenizer	Checkout - Failsafe	No	No	Yes	Yes, 22.5°	Yes	Water color Air bubbles	Hi-adj. DPDT-10 amp (at 110 V)	30-day strip chart recorder (pressure-sensitive paper) (Homogenizer)
Bailey Effluent Monitor Type OT3M with SCM	Failsafe	Yes, electrical (interference filter)	Yes, air curtain	Yes	Yes, 22°	Yes	Suspended solids Air bubbles Oil Droplet Size Source Drift	Lo and hi adj. SPDT or DPDT-5 amp (at 250 V)	30-day strip chart recorder (2 speeds) (Sample conditioning module)
Turner Designs Field Fluorometer Model 10-005	No	No	No	Yes	Yes, 20°	Yes	Air bubbles Particulates	Digital overload output usable for light duty with relays	30-day strip chart recorder (Rustrak) (2-channel)

* Not optional

TABLE A-6. OIL-IN-WATER MONITORS - PRODUCT EVALUATION RATING CRITERIA

Dimensions/ Weight		Rugged		Solid State		Modularized Components		Setup Ease		Water and Salt Spray Resistance		Warmup Time	
1 +	0-5K in^3 2	Yes	5	Yes	5	Yes	5	0-2 hrs	10	NEMA 4	5	0-10 mins	10
	5-10K in^3 1	No	0	No	0	No	0	3-4 hrs	8	NEMA 12	4	10-20 mins	8
	>10K in^3 0							5-6 hrs	6	NEMA 7	4	20-30 mins	6
	0-80 lbs 2							>6 hrs	4	NEMA 3R	4	30-60 mins	4
	80-160 lbs 1									Drip-proof	3	>60 mins	2
	>160 lbs 0												

Sample Flowrate		Price/ Delivery		Temperature Range		Concentration Range	Accuracy		Response Speed		Remote Readout Output	
0->30 gpm	10	0-5K$	10	(Sample, °F)		No. of Operator-Selectable Ranges:	±1	20	<1	25	mVDC	10
0-30 gpm	8	5-10K	8	32-180	10						(customer specified)	
0-10 gpm	6	10-15K	6	35-160, 32-140	8	2 20	±2	16	<10	20		
0-<10 gpm	4	>15K	4	45-150, 40-140, 35-120	6	1 16	±5	12	<30	15	2 ranges	8
		0-1 mo	5	40-90	4		> ±5	8	<60	10		
		1-2 mo	4	(Ambient, °F)		Select widest range, then: subtract -2 if selected range not over 150; subtract -4 if selected range not over 100.					1 range	5
		2-3 mo	3	40-140	5							
		3-4 mo	2	45-130	4							
		4-5 mo	1	50-120	3							
				55-110	2							

Special Circuitry		Self-Calibrating		Automatic Self-Cleaning		Zero Adjustable		Nonlevel Operable		Vibration Insensitive		Interference Avoidance		Alarm Features		Optional Equipment	
Checkout & Failsafe	20	Yes	25	Yes	20	Yes	10	Yes	10	Yes	10	Types		HI/LO	10	Strip-chart Recorder	10
Checkout or Failsafe	10	No	0	Yes, with provision	10	No	0	No	0	No	0	5	30	2 HI's	10		
None	0			Yes (using sample flow)	5							4	25	HI	6		
				No	0							3	20	- - - - -			
												2	15	10 amp	5		
												1	10	5 amp	4		
												0	5	0-3 amp	3		

TABLE A-7. OIL-IN-WATER MONITORS - PRODUCT EVALUATION RATINGS

OIL-IN-WATER MONITORS – PRODUCT EVALUATION RATINGS

	D/W	R	SS	MC	SE	WR	WT	SF	P/D	TR	CR	A	RS	R^2O	SC	SC	ASC	ZA	NO	VI	IA	AF	OE	Total Light Scatter	Total UV Ab-sorption	Total IR Ab-sorption*	Total UV Fluores-cence
Horiba	3	5	5	5	8	5	4	4	10	6	16	16	10	8	20	25	0	10	10	10	30	11	10			231	
CE Invalco	4	5	5	5	6	4	8	4	12	11	14	12	25	5	20	25	20	10	10	10	15	13	10		253		
Biospherics	5	5	5	5	8	5	10	6	14	11	18	16	20	8	20	0	20	10	10	10	25	9	10	250			
Bull & Roberts	5	5	5	5	8	5	6	8	13	9	12	12	20	8	20	25	10	10	10	10	20	9	10		245		
Baird-Atomic	5	5	5	5	10	5	8	4	9	14	16	12	20	5	20	25	20	10	10	10	15	13	10				256
Facet	4	5	5	5	10	4	6	6	11	13	12	20	20	5	20	0	5	10	10	10	10	15	10			216	
Teledyne	1	5	5	5	4	4	2	4	10	11	14	16	15	10	10	0	10	10	10	0	30	14	10		200		
Sigrist	2	5	5	5	4	4	8	4	10	9	16	16	15	10	20	25	20	10	10	10	25	13	10				256
Keene	4	5	5	0	10	5	10	10	12	15	16	20	25	5	20	25	0	10	10	10	15	9	10	251			
ITT	5	5	5	5	6	3	6	8	7	10	14	8	25	8	20	0	5	10	10	10	10	13	10	201			
SRS	5	5	5	5	8	5	10	8	15	11	12	12	25	5	20	0	0	10	10	10	15	11	10	217			
Bailey	3	5	5	5	4	5	6	4	10	7	12	16	25	5	10	25	20	10	10	10	25	14	10				246
Turner	5	5	5	0	10	3	10	4	12	9	12	16	20	8	0	0	0	10	10	10	15	6	10				180

* The Horiba detector uses a procedure involving solvent extraction followed by IR absorption, while the Facet device uses near-IR absorption directly on the sample stream.

can be determined by devices utilizing ultraviolet absorption and fluorescence. In addition, UV fluorescence can also be used to detect aromatic compounds in the free oil phase.

A users evaluation of the top-rated devices using the four principles of operation, that is, UV absorption, UV fluorescence, extraction with IR absorption, and light scatter, was conducted to provide additional data for the study. When requests were made of representatives of top-rated Baird-Atomic Inc., Biospherics Inc., and Keene Corp. for up-to-date users lists and they were unresponsive, other manufacturers were contacted and their devices, in turn, were substituted in the users evaluation.

At the same time, since the two remaining light scatter devices were among the lowest rated devices in the product evaluation (see Table A-7), it was deemed appropriate to eliminate light scatter as a principle of operation in the detection system. The users contacted are listed in Table A-8. The Bailey and Turner devices were included per request of the EPA Project Officer. The 15 factors for which users' comments were solicited and the rating criteria are found in Table A-9. Tabulation of the users evaluation ratings, listed in Table A-10, shows the Sigrist Fluorescence Meter as the top user-rated device with an average value of 78. Total overall ratings of 334 for the Sigrist, 308 for the CE Invalco D.O.W. Monitor, and 282 for the Horiba Model OCMA-32A Oil Content Monitor were obtained as the highest overall rated devices, one for each of the three remaining principles of operation. Therefore, these three devices are recommended for incorporation in the multi-detector petroleum oil-in-water monitoring system to be developed under subsequent phases of work.

The capability of an oil-in-water monitoring system built from commercially available devices to accurately quantify petroleum oil in water depends on its ability to respond to all oil components while eliminating contributions from various interfering substances. It is recognized, though, that due to the complexity of crude oil and similarities between components of crude oil and some interfering substances, such as animal and vegetable oils, a prototype system formed from commercially available devices will have to be calibrated with a known oil, if it is to be a viable and practical system. In this regard, a desk-top analysis of the components of petroleum with emphasis on the soluble-in-water nonhydrocarbon oil fraction shows that most nonhydrocarbon species containing sulfur and oxygen would escape detection by present commercially available devices. However, if interfering substances are limited in number, a system developed from two or more commercial devices and calibrated with a known oil should be a definite improvement over any single commercial device.

NOTE: The data reported in the Oil Monitor Survey was obtained over a period beginning in early 1978 and terminating in mid-1979. Any subsequently developed oil monitoring instrumentation will not be found in this study. In addition, certain information contained herein, such as price and delivery data, is extremely dated. The Oil Monitor Survey was formalized in January 1980 and included with the Experimental Evaluation Program Plan transmitted to the EPA Project Officer.

TABLE A-8. OIL-IN-WATER MONITORS - USERS CONTACTED FOR INFORMATION*

Device	1	2
Horiba	Chevron Shipping Co. San Francisco, CA 94105 (Dave Pritchard) (415) 894-2393	Hyde Products Westlake, OH 44145 (Brian Casey) (216) 871-4885
Sigrist	EPA Pilot Plant Lebanon, OH 45036 (Walter Schuk) (513) 684-7635	Dow Chemical Co. Pittsburg, CA 94565 (Rick Brooks) (415) 432-5000
CE Invalco	Technical Systems, Inc. Lynnwood, WA (Jim Gately) (206) 775-5696	General Motors Corp. Detroit Diesel Division Indianapolis, IN (Ray Starnes) (317) 244-1511
Bailey	Hanna Mining Co. Cleveland, OH (Bing Miller) (216) 523-3111	Louisiana Power & Light Nine Mile Point, LA (Miller Justice) (504) 436-3811
Turner	Endeco Marion, MA 02738 (Ed Brainard) (617) 748-0366	IEA, Inc. South Burlington, VT 05401 (Kathy Cutting) (802) 864-6336

* Representatives of Baird-Atomic Inc., Biospherics Inc., and Keene Corporation were contacted for up-to-date users lists, but they were not responsive to the requests.

TABLE A-9. OIL-IN-WATER MONITORS - USERS EVALUATION

User Contacted*	Horiba		Sigrist		CE Invalco		Bailey		Turner	
	1	2	1	2	1	2	1	2	1	2
Overall Impression	P	A	G	G	P	P	A	G	G	G
Repairs	G	G	G	G	G	P	A	G	G	G
Setup Ease	A	A	G	G	P	P	P	A	G	G
Warmup	G	G	G	G	G	G	A	A	G	G
Temperature Range	P	G	G	G	G	G	G	G	G	G
Concentration Range	G	P	G	G	A	G	G	A	A	A
Accuracy	G	G	G	G	P	P	G	G	G	G
Response Speed	G	G	G	G	G	G	G	G	G	G
Special Circuitry	P	G	G	A	A	G	A	G	G	A
Calibration	G	A	G	G	P	P	G	G	G	G
Cleaning	P	P	G	G	A	G	G	P	G	G
Vibrations	G	A	G	G	G	A	G	G	G	G
Interferences	A	P	G	G	G	G	G	G	G	G
Alarm System	A	A	G	A	G	G	G	G	P	P
Flowrate	P	P	G	G	G	G	P	P	G	G

Users Evaluation Rating Criteria:

Rating	Value
G - Good	5 (10 for Overall Impression)
A - Average	3 (6 for Overall Impression)
P - Poor	1 (2 for Overall Impression)

* See Oil-in-Water Monitors - Users Contacted for information (Table A-8).

TABLE A-10. OIL-IN-WATER MONITORS - USERS EVALUATION RATINGS

Device	User	OI	R	SE	W	TR	CR	A	RS	SC	Ca	Cl	V	I	AS	FR	Total
Horiba	1	2	5	3	5	1	5	5	5	1	5	1	5	3	3	1	50
	2	6	5	3	5	5	1	5	5	5	3	1	3	1	3	1	52
Sigrist	1	10	5	5	5	5	5	5	5	5	5	5	5	5	5	5	80
	2	10	5	5	5	5	5	5	5	3	5	5	5	5	3	5	76
CE Invalco	1	2	5	1	5	5	3	1	5	3	1	3	5	5	5	5	54
	2	2	1	1	5	5	5	3	5	5	1	5	3	5	5	5	56
Bailey	1	6	3	1	3	5	5	5	5	3	5	5	5	5	5	1	62
	2	10	5	3	3	5	3	5	5	3	5	1	5	5	5	1	64
Turner	1	10	5	5	5	5	3	5	5	5	5	5	5	5	1	5	74
	2	10	5	5	5	5	3	5	5	3	5	5	5	5	1	5	72